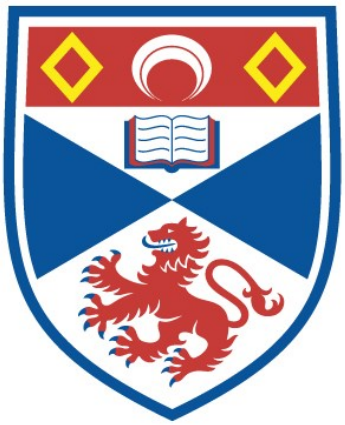
# DIFFUSION CONTROLLED OXIDATION AND STABILISATION OF POLYOLEFINS

Stuart Paterson Fairgrieve

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1984

# DIFFUSION CONTROLLED OXIDATION AND STABILISATION OF POLYOLEFINS

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St.Andrews

by

Stuart Paterson Fairgrieve, M.Sc.

December 1983

United College of St.Salvator

and St.Leonard, St.Andrews.

## DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by me, and that it has not been submitted in any previous application for a higher degree.

This thesis describes results of research carried out in the Department of Chemistry, United College of St.Salvator and St. Leonard, University of St.Andrews, under the supervision of Dr. J.R.MacCallum since the 1st October 1980.

Stuart P. Fairgrieve

CERTIFICATE

I hereby certify that Stuart Paterson Fairgrieve has spent twelve terms of research under my supervision, has fulfilled the conditions of Ordinance No.12 and resolution of the University Court, No.1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Dr. James R. MacCallum

ACKNOWLEDGEMENTS

I should like to record my gratitude to Dr.J.R.MacCallum for his help and encouragement in all parts of this work.

I am indebted to the Ministry of Defence, PERME, for a Research Studentship to finance this work from 1980 - 83, and to Prof. Lord Tedder and Prof. P.A.H.Wyatt for providing research facilities during this period.

I wish to thank all the teaching and technical staff of the Chemistry Department for their assistance, in particular Mrs. S.Johnson (librarian), Mrs. M.Smith (NMR), Mr. R.Cathcart (workshop), and Mr. J.Ward (electronics).

"....the truth , unblemished with marvels"

Tacitus "Annals of Imperial Rome"

CONTENTS

TO AUDREY

## SUMMARY

A mathematical model was derived for the oxidation behaviour of a polymer film, taking into account both diffusion free and diffusion controlled kinetics. Comparison with experimental results showed excellent agreement. Expressions were derived from this model for the reaction induction time, and the limiting thickness of film at which diffusion effects become important.

Investigation of the photostabilisation mechanism of Hindered Amine Light Stabilisers was undertaken. After experimental investigation of numerous proposed stabilisation processes, and their rejection, a reaction scheme was proposed involving the scavenging of trace transition metal ions in the polymer matrix.

# 1 BACKGROUND.

## 1:1 Photo-oxidation.

In order for a photochemical reaction to take place under normal terrestrial conditions, the substance undergoing reaction must contain groups capable of absorbing energy in the range of 300-800nm, which is the wavelength band of sunlight reaching the earths surface. These groups are known as chromophores.

Absorbance of energy causes the chromophore to become electronically excited, and it may then undergo a chemical or physical change itself, or may transfer this energy to another group which then undergoes transformation. The usual result of such an energy absorption is the homolytic scission of a chemical bond to produce free-radical species. These species are extremely reactive, and may undergo a number of reactions - recombination, hydrogen abstraction, or addition with oxygen. Products can themselves react further. A simplified reaction scheme for photo-oxidation of a hydrocarbon is given below :-

$$RH \longrightarrow R.$$

$$R. + O_2 \longrightarrow ROO.$$

$$ROO. + RH \longrightarrow ROOH + R. \qquad \text{Propagation}$$

$$ROOH \longrightarrow RO. + .OH$$

$$RO. + RH \longrightarrow ROH + .OH$$

$$HO. + RH \longrightarrow H_2O + R. \qquad \text{Branching}$$

$$2\ ROO. \longrightarrow ROOR + O_2{}^1$$

$$2RO. \longrightarrow ROOR$$

$$2R. \longrightarrow R - R \qquad \text{Termination}$$

Among the more important hydrocarbons subject to the above reaction scheme are the man-made polymers. Photo-oxidation, causing as it does the loss of physical properties and discolouration of finished polymeric articles, is a major problem for the plastics industry and a great deal of effort has gone into the understanding and combating of this problem [1].

The degradation behaviour of some polymers under photo-oxidative conditions is relatively easy to understand as they contain chromophore groups, e.g. poly(styrene), poly(vinylnaphthalene), poly(acetylene); but others such as poly(ethylene) and poly(propylene) would appear to contain no chromophore capable of absorbing radiation in the range of terrestrial sunlight, and yet the useful lifetime of such polymers under photo-oxidising conditions is very short [2]. The answer to this dilemma lies in the fact that all polymer systems contain impurities of various types, either in the matrix, or as part of the polymer chain.

Impurities in polymers come from various sources and can take various forms :-

a) Impure starting materials- this may introduce a serendipitous copolymer unit into the polymer chain, creating either a weak link in the chain, or providing a chromophore.

b) Chain branching- again may lead to weaker bonds.

c) Catalyst residues- transition metal catalysts are commonly used in the polymerisation of olefins [2], and can be actively involved in hydrocarbon photo-oxidation [3]. These metal species may appear free, or bonded to the macromolecular chain.

d) Oxygen containing groups- both during polymerisation, and during susequent processing, oxygen will be present to some extent, and this may lead to the appearance of hydroperoxide, carbonyl, and acid groups in the polymer. Hydroperoxides in particular, are considered to be one of the main initiating groups in polyolefin photo-oxidation [2]. Carbonyls, particularly ketones, are also known to be important species in photo-oxidation [4].

e) Impurities picked up during processing- During the processing of a raw polymer into a finished film, fibre, or other article, the material will come into contact with machinery, and thus pick up more metal ions to add to those already present due to catalyst residues. Microscopic metal fragments have been observed in poly(propylene) from this source [5].

It has also been suggested [2] that emission spectroscopic results point towards there being polynuclear aromatic compounds present in poly(propylene), absorbed from atmospheric pollution, although it is only fair to say that some authors disagree with this identification [6].

f) Deliberate additives- We will not go into this in any great detail, but the addition of organic pigments will obviously cause a polymer to absorb more light, and with energy transfer processes operating this may cause further degradation. One particular additive worth mentioning is the $TiO_2$ or ZnO delustrant added to many polymers. $TiO_2$ is known to be photochemically active, as is ZnO, and polyolefin degradation has been shown [7] to be accelerated when either of these pigments is added.

## 1:2 Photo-stabilisation

Some, or all, of the above impurities are always present in polymer systems to a greater or lesser extent. Physical methods, such as purification of starting materials, low temperature processing, or purification of final products are all practically, or commercially, inapplicable. In any case, purification by these means does not get rid of all impurities. The only alternative is stabilisation.

Stabilisation involves the incorporation of some chemical into the polymer matrix which either prevents the onset or degradation processes, or in some way eliminates products of primary photodegradation before the onset of discolouration or deterioration of physical properties.

The means whereby such stabilisers can prevent degradation of polymers can be broken down into the following categories:-

a)Screening of detrimental light.

b)Quenching of electronically excited states.

c)Non-radical decomposition of hydroperoxide.

d)Complexing of trace metals.

e)Interception of photo-oxidation products.

f)Radical scavenging

g)Transformation of stabiliser into a product capable of fulfilling one or more of the above functions.

a) Screening The screening of a polymer against the effects of incident light could be simply achieved by laminating with metals to acheive a highly reflective surface, or by incorporating a substance which will absorb all light, such as carbon black. However, if a clear film, or a fibre is required, these methods are obviously of little use. Since the small percentage of terrestrial sunlight in the ultraviolet region of the spectrum has been shown to be energetically resposible for most polyolefin photodegradation processes [8], early work on stabilisation concentrated on compounds which absorbed only in this region and were transparent to visible light, such as the benzotriazoles and 2- hydroxybenzophenones [9]. The limitation of this approach is that in fibres and thin films, which are the most vulnerable articles to photo-oxidation, there is simply not enough of the absorber present to give adequate protection by screening alone.The fact that these materials are still in widespread use results from the ability of these compounds to photostabilise polymers by other pathways.

b) Quenching of electronically excited states The excitation of chromophores in a polymer by light will produce electronically excited states (EES). In general, the excited state of a chromophore may react, fragment, return to the ground state by physical routes, or transfer its excess energy to a stabiliser or to some other acceptor species. If energy transfer to the stabiliser can compete with the combination of other processes, the chromophore is deactivated and the polymer stabilised [10].

Electronic energy transfer (EET) involves interaction, either radiatively or non-radiatively, between an electronically excited chromophore (Donor) and a ground state stabiliser molecule (Acceptor), such that the donor is de-excited and the acceptor raised to an EES [11]. Non-radiative mechanisms are most relevant in this context, and may occur by two processes. Coulombic, or long range, transfer [12] occurs when the excited chromophore and the quenching species are separated by 1-10nm, but there must be appreciable overlap between donor emission and acceptor absorption spectra. Alternatively, exchange, or collisional, transfer [13] requires physical contact between donor and acceptor.

Quenching of excited carbonyl groups has been shown to occur using benzotriazoles [14], hydroxybenzophenones [15], and to a lesser extent with Ni(II) chelates [16]. The efficiency, and indeed the mechanism, of this stabilisation pathway is still a matter of controversy.

The absence of structure in the absorption spectra of peroxides and hydroperoxides indicates that transient excited states do not exist upon UV irradiation; only instantaneous dissociation of the O - O bond occurs. This implies that the quenching of these species by either of the above mechanisms is impossible.

Quenching of EES of polynuclear aromatics would prevent oxidation of these compounds to endoperoxides and aromatic ketones, which can then act as initiators to provide radical species [2]. Ni(II) chelates can quench the triplet EES of anthracene [17], although their efficiency fluctuates greatly with ligand species 2 (2'-hydroxy-5'-methylphenyl) - benzotriazole has been shown to be a good quencher of anthracene singlets [18].

c) Non-radical Decomposition of Hydroperoxide As may be seen from the reaction cycle already described, hydroperoxides are important intermediates in the oxidation of hydrocarbons. In the photo-oxidation of polyolefins they have been considered to be primary initiators of photoreactions [2]. To remove ROOH groups from the autoxidation cycle it would be best to do so via a rapid dark reaction which does not release free - radicals. Provided a hydroperoxide decomposer has adequate mobility and good UV stability, hydroperoxide scavenging must be expected to play a vital role in polymer UV stabilisation [19]. Hydroperoxides possess long chemical half-lives due to low quantum yield and weak UV absorption [19], so there is an appreciable time interval during which a stabiliser might diffuse

to a hydroperoxide site and decompose ROOH before photolysis can occour.

Several Ni(II) and Zn(II) chelates [19,20] have been shown to be effective decomposers of ROOH in poly(propylene), while many sulphur compounds show similar efficiency [21].

d) Complexation of Trace Metals Ti catalyst residues appear to be potentially important sources of initiation for the photo-oxidation of polyolefins [2], inclusion of Fe salts in poly(propylene) also leads to accelerated degradation [22]. Very little published material exists on the ability of additives to deactivate metal impurities in polymers, although oximes [23], bisphenols [24], and epoxides [25] have been shown to interact with Ti(III) and Ti(IV).

Uri [26] has noted the ability of transition metal ions, in very low concentrations, to greatly enhance the rate of photo-oxidation of hydrocarbons, while Lunak et al [27] have provided evidence to suggest that the photolysis of hydrogen peroxide does not proceed in the absence of transition metal impurities. In order to explain the above observations Black [28] has proposed a hydroperoxide-metal complex as the initiating species. This evidence suggests that an efficient metal complexing agent, provided it is light stable, would also be a possible polymer photostabiliser.

e) Interception of Photo-oxidation Products. The influence of certain molecular products formed during the photo-oxidation of polyolefins upon the subsequent process has been realised. Out of a variety of products formed, only the hydroperoxides are unanimously cited as being of primary importance [2,29,30]. The role of ketones is still a matter of discussion, carbonyls being proposed as initiating species via an excited state quenching by hydroperoxide [4], while the effect of other oxidised products such as aldehydes, acids, and peracids on the photo-oxidation has not been assessed.

f) Radical Scavenging A simplified reaction scheme for the photo-oxidation of poly(propylene) is shown below :-

$$PPH \longrightarrow PP.$$

$$PP. + O-O \longrightarrow PPOO.$$

$$PPOO. + PPH \longrightarrow PPOOH + PP.$$

$$PPOOH \longrightarrow PPO. + .OH$$

$$PPO. + PPH \longrightarrow PPOH + PP.$$

$$2\ PPOO. \longrightarrow \text{products}$$

As may be seen, poly(propylene) photo-oxidation involves long lived $PPO_2.$ radicals, shorter lived PPO. and PP. radicals, and very short lived .OH radicals [2]. The scavenging of any of these radical species, but particularly the initial PP. radicals, to give non reactive, photostable, products will obviously contribute to stabilisation of the polymer [31].

Hindered phenols [32,33] have been shown to be effective scavengers of PPOO., while transition metal chelates are put forward as possible scavengers of ROO., RO., or R. species [19]. Nitroxide radicals [34] and oximes [35] are erfective UV stabilisers and are thought to operate via an alkyl radical trapping mechanism.

g) Additive Transformation Most stabiliser systems, when they do undergo change, do so for the worse. Long exposure to sunlight may lead to photoproducts which are themselves coloured, or to bond scission to produce radicals or harmful chromophoric species.

Hindered phenols [36] however, can react with peroxy radicals to produce relatively stable radical species which themselves will react with another peroxy radical. This is a limited example of this phenomenon, as the reaction is irreversible, and the second radical encountered leads to a quinone type species which may act as a sensitiser.

Looking at the above descriptions, it is immediately obvious that many stabilisers operate by more than one mechanism, and the complete elucidation of the various stabilisation pathways used can be extremely complex.

In looking for a viable mechanism, it must always be bourne in mind the type of environment in which the additive has to be effective. The crystallinity and tacticity of the polymer will be subject to a great deal of variation, even within one type, and this non-homogeneous environment must be taken into account when applying results from the solution phase, or from more ordered solids. The variation in crystallinity, in particular, means that the concentration of any additive will be subject to variation, since it will tend to remain in amorphous regions [37]. Photo-oxidation of a polyolefin takes place in the amorphous regions of the matrix [38], therefore this can be a help rather than a hinderance

Again due to the inhomogeneous nature and glassy character of the medium, the diffusion of both oxygen [39], and stabiliser [40], will have to be taken into account.

In recent years the search has gone on for further new classes of stabiliser. The most promising find of recent years has been the family of stabilisers based on 2,2,6,6-Tetramethylpiperidine (TMP), and derivatives thereof. These are known as Hindered Amine Light Stabilisers (HALS). It was the purpose of this study to attempt to elucidate the mechanism whereby these additives achieve their remarkable photostabilising ability.

# 2 INTRODUCTION

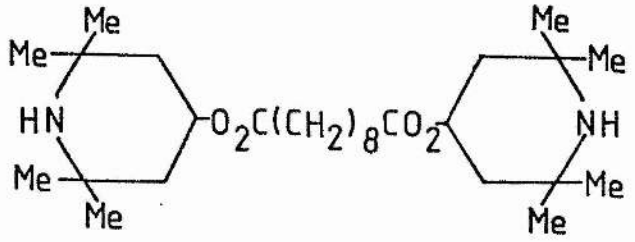
## 2:1 Discovery of HALS

In the late 1960's, the search for new classes of polymer photostabilisers led to the consideration of stable nitroxide radicals as possible additives. The compounds were already well known and characterised from their use as spin probes [41], and their use as additives was originally considered on the basis of their ability to trap radical species present during the oxidation of hydrocarbons [42]. The remarkable efficiency of these compounds in preventing polymer photo-oxidation was noted [43],but they have the disadvantage of intense colouration - yellow to red - which prevents their commercial usage.

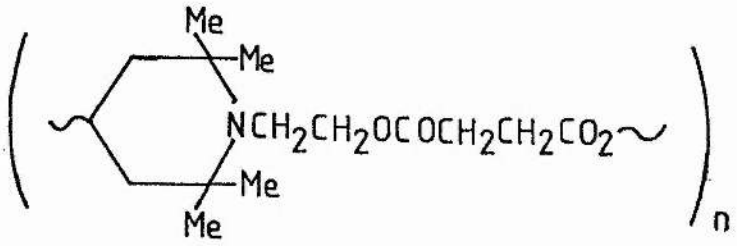
Somewhat surprisingly it was soon noted by chemists of the Sankyo Company, that not only the nitroxide radicals, but specific amines, could exhibit high photostabilising ability [44]. The first commercial polymer stabiliser of this type was based on the hindered amine 2,2,6,6 - Tetramethylpiperidine, this being incorporated into a larger molecule (Bis (2,2,6,6 - tetramethylpiperidine) sebacate) to prevent loss by volatilisation, and known by the commercial name of Tinuvin 770. Almost all commercial stabilisers of this type are based on the 2,2,6,6 - Tetramethylpiperidine (TMP) nucleus, and this has given them the general name of hindered amine light stabilisers (HALS).

Figure 2.1

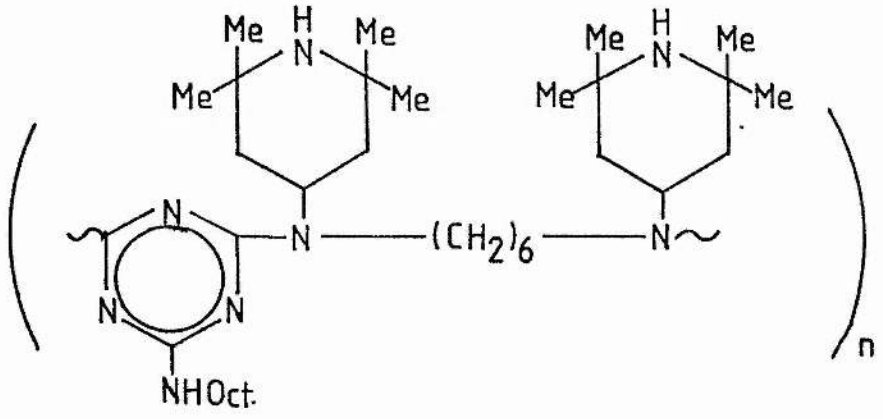
Examples of commercially available HALS.




TINUVIN 770




TINUVIN 622




CHIMASSORB 944

Present trends in the field of commercial HALS are in the direction of increased molecular weight [45], polymeric stabilisers [46], incorporation of HALS into the polymer backbone [47], and inclusion of other stabilising species into the HALS molecule [48]. Tertiary amines, i.e. 1 - alkyl - 2,2,6,6 - tetramethylpiperidines are also being used commercially as successful photostabilisers for polymers [48,49,50] (See Figure 2.1 for a representative sample of HALS in commercial use.)

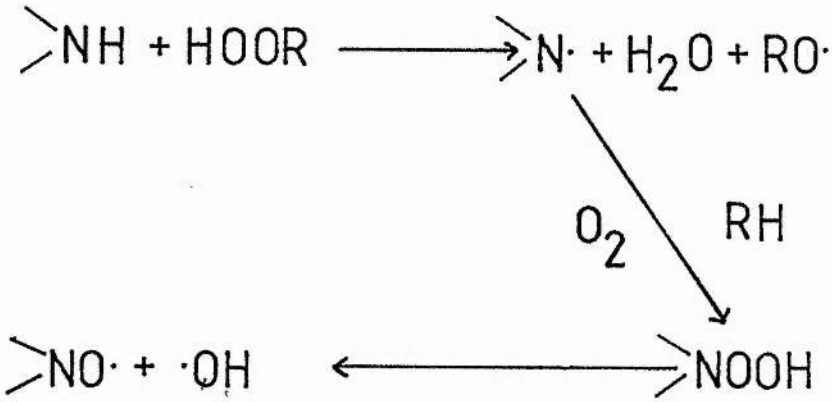
Although HALS have been in commercial use for almost a decade, the mechanism of their stabilising action has not yet been fully elucidated. The picture so far is of a complex stabilisation mechanism involving multifunctional behaviour, and conversion of the parent amine into other stabilising species. A great deal of literature has been published concerning the stabilisation mechanism involved in the use of HALS and derivatives thereof, and we will now proceed to examine the ways in which HALS may be converted to other species, and how the amines and these derivatives can act as photostabilisers for polyolefins.

## 2:2 Interconversion of HALS Derivatives

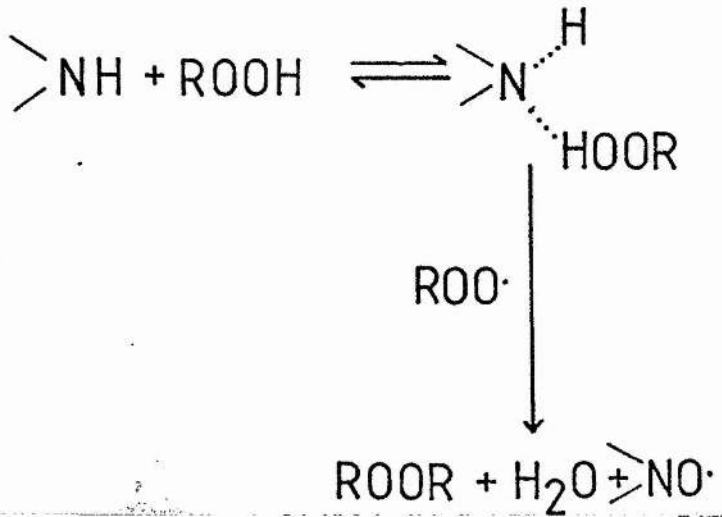
As has been noted in Chapter 1, there are few known stabilisers for which conversion of the original compound to stabilising species is significant. However, in the case of the HALS there is a great deal of evidence to suggest that this particular pathway is crucial to their success, and therefore we shall treat this as a seperate topic, then go on to assess the ability of the HALS and their derivatives to perform any of the

functions mentioned.

In studies of photo-oxidation of polyolefins containing HALS, it was noted [51,52] that the original amine appears to be rapidly lost, and a low, steady state, concentration of nitroxide radical is formed - approximately 2% [53] of the original additive concentration. The reaction whereby this conversion is achieved was proposed by Chakraborty and Scott [54] to be due to reaction of HALS with hydroperoxide followed by reaction with the polymer under oxidising conditions :-

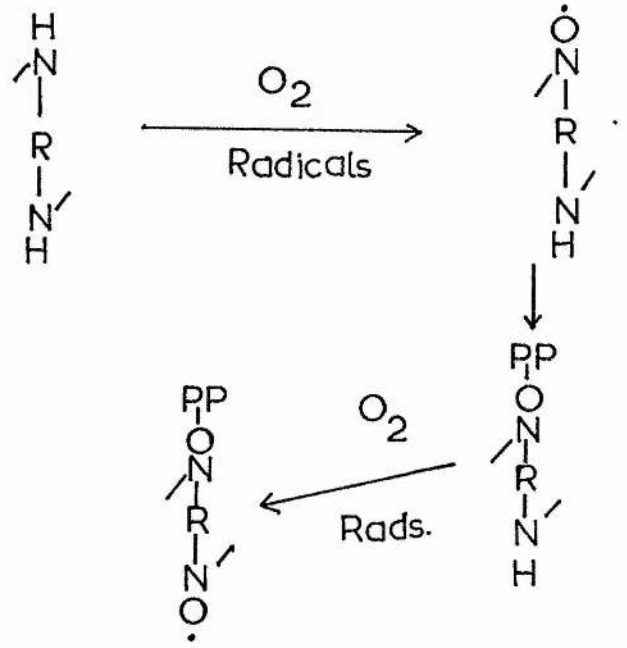



However, as is immediately apparent, this scheme creates many radical species which are capable of undergoing H - abstraction reactions, and this would appear to make the HALS operate as an accelerator, rather than an inhibitor, of photo-oxidation. Sedlar et al [55] suggested that, due to the high basicity of HALS, these compounds would associate with acidic groups such as hydroperoxides in the polymer, and they proposed the following scheme [56] :-



It is important to note at this point that the reaction between HALS and ROOH is stoichiometric and not catalytic.

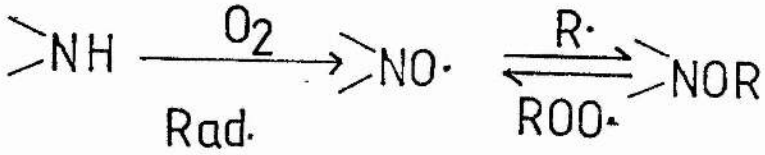
Carlsson et al [57] have suggested that the nitroxide, like the parent amine, may be able to associate with hydroperoxide, and thus be available for further, radical trapping, reactions in oxidised areas of a polymer. The residual level of NO. in polyolefins, even taking this possibility into account, is not enough to explain the excellent photostabilisng behaviour of the HALS [51]. Nitroxides can act as alkyl radical traps [52], and some form of efficient regenerative mechanism or conversion of the nitroxide to yet another stabiliser species is required. Evidence for the ability of nitroxides to react with polymeric alkyl radicals comes from a series of experiments on poly(propylene) stabilised by a bifunctional HALS carried out by Hodgeman [52] for which the following reaction scheme was proposed :-



Further results from the same author [53] show that a maximum of 20% of the radicals formed are grafted onto the polymer; this is very different from the figure of 80% of the total additive concentration grafted to the polymer suggested by Carlsson et al [58], although the latter figure was obtained by indirect means.

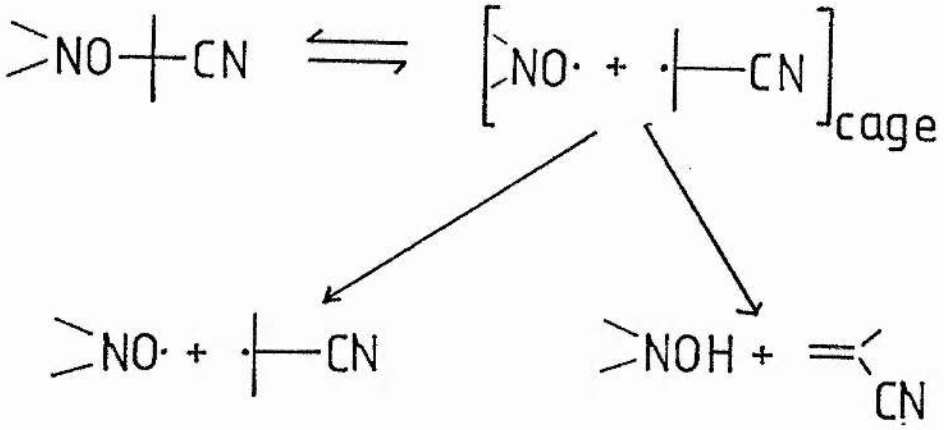
In an early paper on the subject, Shilov [59] suggested that nitroxide radicals might be regenerated from the polymer grafted hydroxylamine ethers via reaction with polymer hydroperoxy radicals :-

Hodgeman [53] also proposed such a mechanism, suggesting the general scheme :-

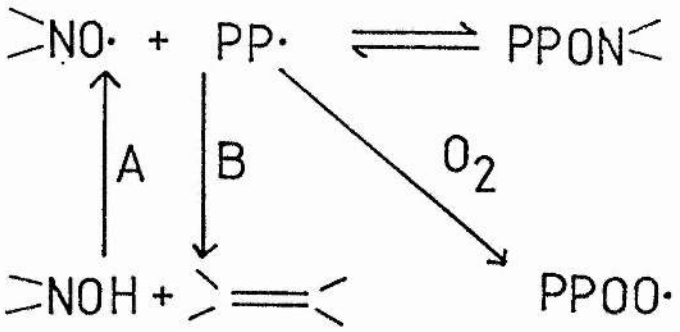


Even combining the reaction between R. and NO., followed by NOR reacting with ROO. to regenerate the radical, the extent of photostabilisation associated with HALS is still not fully explained. Chakraborty and Scott [60] noted that, during thermal and mechanical degradation of polyolefins stabilised with HALS, a hydroxylamine intermediate was formed. Grattan et al [61], using

a model system under mild thermal degradation conditions, proposed the following scheme :-




In the presence of $O_2$ the nitroxide is regenerated, without $O_2$ (or another radical scavenger) a hydroxylamine is formed. It was also noted that decomposition took place 50 times faster in the presence of a radical scavenger, such as $O_2$. Bagheri et al [62] have recently produced evidence to suggest that hydroxylamines may play an important role both during polymer processing and in the course of photo-oxidation. They have produced a scheme whereby the hydroxylamine is shown to be of crucial importance as a regenerative intermeddiate. Previous work [63] on thermal autoxidation inhibition by hydroxylamines suggests that they are also powerful scavengers of peroxy radicals. The reaction sequence proposed by Bagheri [62] is as follows :-



The relative rates of reactions A and B will determine the ratio of nitroxide to hydroxylamine in the system.

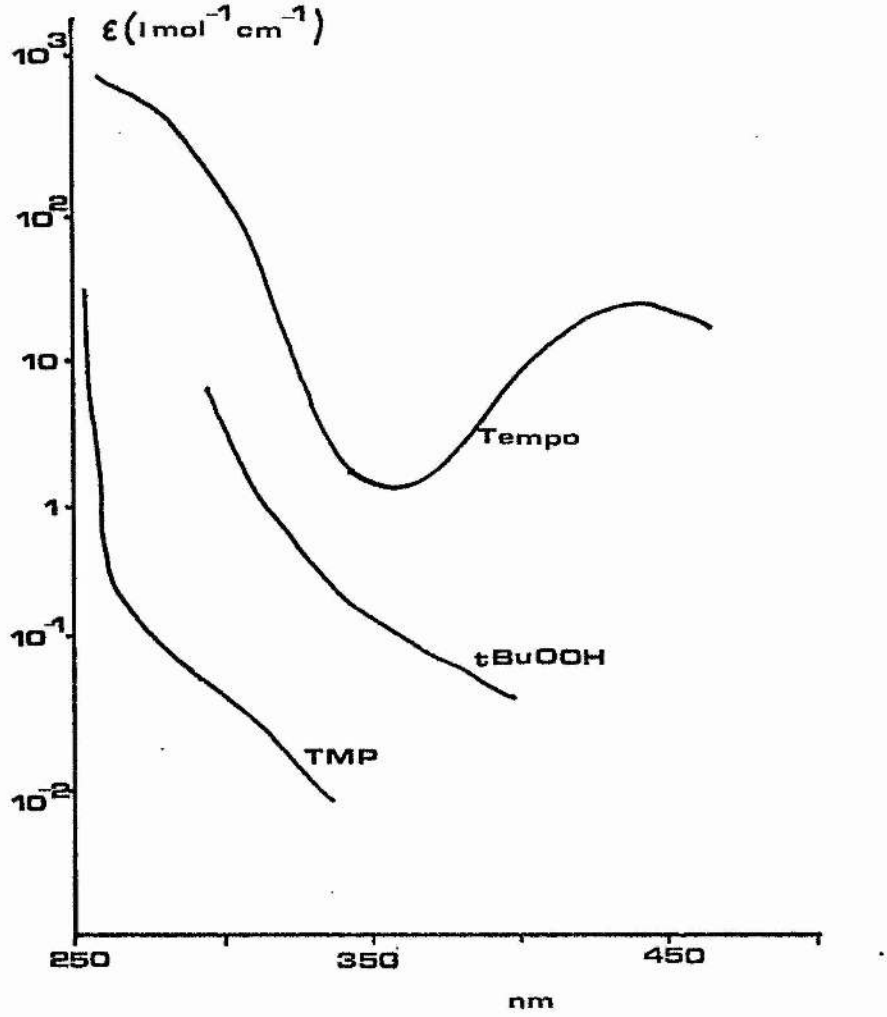
The use of tertiary hindered amines as successful polymer photostabilisers poses a problem as far as interconversion goes. Felder [64] has shown that poly(propylene) samples containing N - alkyl substituted HALS attain a steady state population of NO., but at much lower concentration than that for secondary amines. This may result from a slower rate of reaction in the scheme suggested by Sedlar [56] and shown above. Chinese authors [65] have suggested a two step process, and Jensen et al [66] propose a mechanism involving attack by an O - centred radical on the tertiary HALS to convert it to a secondary species, and subsequent reaction of the secondary amine in the above schemes.

## 2:3 Photostabilisation Mechanisms of HALS

a) Screening Comparing the UV / Visible absorption spectra of 2,2,6,6 - tetramethylpiperidine (TMP) and t-Butyl hydroperoxide (t-BuOOH) (Figure 2.2), it is clear that the possibility of a hindered amine acting as a simple UV screener must be ruled out. To obtain efficient screening with regard to hydroperoxide, the value of the extinction coefficient for TMP would have to be at least three orders of magnitude higher in the region 300-350nm. A similar situation exists for the nitroxide TMPO in the low wavelength region. At higher wavelengths, the nitroxide absorbs considerably more light than the hydroperoxide. Thus, the electronic excitation of the nitroxide may take place, leading to a number of possibly undesirable

Figure 2.2

Comparison of the UV/Visible absorption spectrum of 2,2,6,6-tetramethylpiperidine and its nitroxide derivitive with that of tBuOOH.



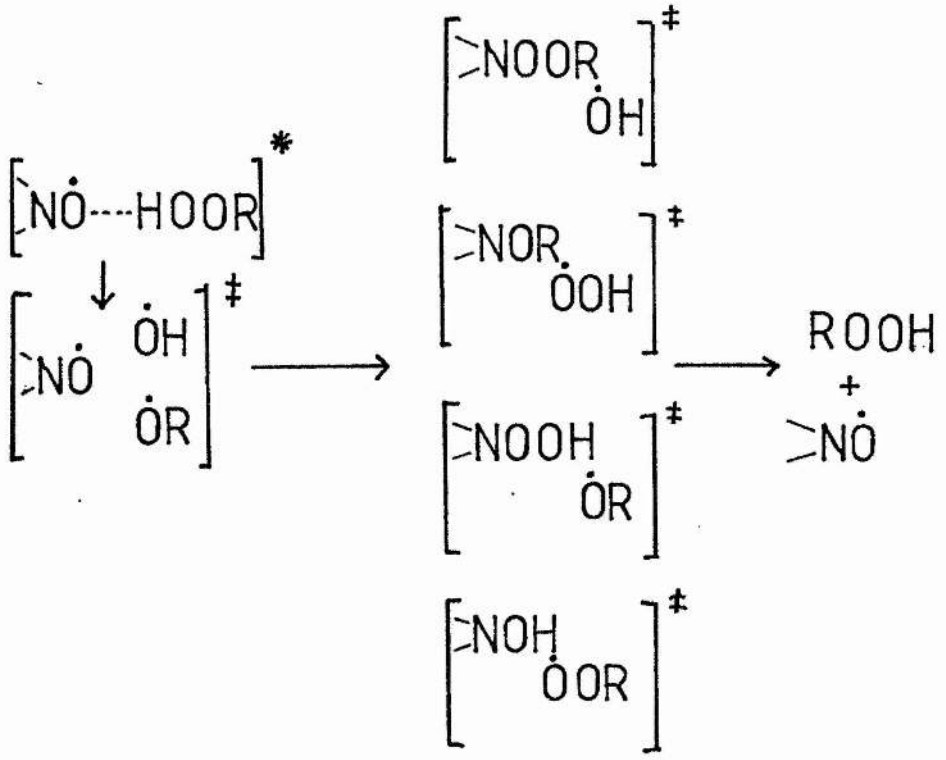
photochemical reactions.

b) Excited State Quenching Similarly to nitric oxide, nitroxide radicals are paramagnetic, and are good electron acceptors. This enables them to quench both singlet and triplet EES, in theory. Investigators have shown [31,67,68,69,70] that, while hindered amines themselves are poor quenchers of EES and singlet oxygen, the derived nitroxides are capable of acting as moderately efficient quenchers of EES of carbonyl and aromatic compounds, in the liquid phase.

The long distance quenching of EES by nitroxides cannot, however, be considered of primary importance. Heller and Blattmann [31] have calculated that an effective long - distance quencher has to possess the absorption characteristics of an efficient UV screener; this is clearly not the case.

In the case of collisional mode quenching, the situation is not so clear cut. Although the calculated [31] concentration required to obtain an appreciable quenching efficiency is far in excess of commercial additive concentrations, and much higher than the residual level of nitroxide thought to be present in a photo-oxidising polymer system, there is the possibility of local concentration of these radicals. In addition, an association between nitroxyls and ROOH has been reported both in solution [57] and in polymer matrix [71], and this may be of particular importance to the fate of a hydroperoxide excited state.

As noted already, hydroperoxides have dissociative excited states, i.e. bond rupture occours before the energy absorbed can be dissipated in any other way. However, if the hydroperoxide is in association with a nitroxide, the possibility exists of its being able to dissipate the energy physically and re-emerge unchanged. A scheme for this was suggested by Sedlar [72]




The overall effect would then appear as a chemical quenching of hydroperoxide by the nitroxide.

c) Decomposition of Hydroperoxide Some controversy surrounds the ability of HALS to actively decompose ROOH species to non-chromophoric products. Usilton and Patel [73], and Grattan et al [74] have both suggested that decomposition of ROOH

was a plausible mechanism. Carlsson et al [75] reported on the ability of HALS to rapidly decompose poly(propylene) hydroperoxides, while Dulog and Bleher [76] have noted that nitroxides contribute to the decomposition of ROOH, although the latter work was carried out at elevated temperatures. The results of Carlsson [75] have been called into question by Sedlar et al [56], and the same authors [77] have shown there to be no significant effect of HALS on ROOH decomposition. It must be remembered however that in a polymer matrix the results from a solution phase experiment may not be applicable, thus the question of HALS ability to decompose ROOH remains open.

d) Complexing of Trace Metals As previously stated, little work has been carried out on the effect of trace metals on the photo-oxidation of polyolefins, and less has been published on the ability of specific stabilisers to interact with metal ions. Sedlar et al [56] have reported finding that HALS interfere with a ROOH analysis method using Fe(III). Experiments on the photo-oxidative degradation of tetramethylnonane carried out in the presence of $Ti(OBu)_4$ [78], and HALS, noted suppression of the autocatalytic nature of the reaction. Results suggest that HALS, although probably unable to inhibit the initiation due to tBuO. radicals, is intercepting the species causing autoacceleration.

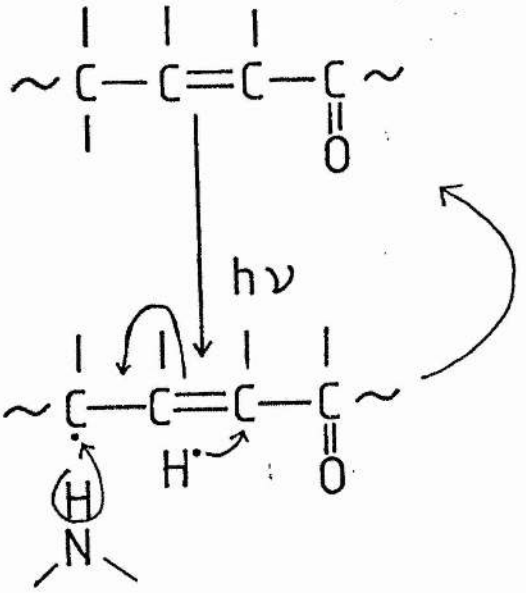
e) Interception of Molecular Products The influence of certain molecular products, formed during the photo-oxidation of polyolefins, upon the subsequent degradation process has been realised. Of the variety of products formed, we have already noted that only the hydroperoxides are generally accepted as initiators of primary importance [2]. As has already been

detailed in Section 2:2, interaction between HALS and ROOH is considered by some authors to be of fundamental importance to the photostabilisation of polyolefins [55,56,57]. It is thus suggested that HALS, due to their high bacisity, are capable of intercepting acidic products of polyolefin photo-oxidation either via H - bonding [55] or via ammonium salt formation [56]. This association will in turn lead to a strong local concentration of the stabilising species in the most vulnerable oxidised areas.

Photolysis of this ROOH - HALS association will result initially in formation of alkoxy and hydroxyl radicals, as would happen in the case of ROOH alone, but with the proximity of HALS the radicals so formed might be expected to undergo reactions to produce non-radical species such as hydroxylamines and hydroxylamine ethers which, as detailed previously, may themselves act as stabilising species. Chien [79] has noted that hydroperoxides in poly(propylene) tend to hydrogen bond in 1,3 fashion, therefore any complexation between HALS and ROOH will have to compete with this. The values of association constants for model systems will be examined later.

Allen and McKellar [80] have suggested that degradation of polyolefins might be due in part to the action of $\alpha,\beta$ - unsaturated ketones. Following absorption of a photon, these are isomerised to $\alpha,\gamma$ - unsaturated species, which may then proceed to give radicals and further unsaturated species via the well known Norrish type I & II reactions [81]. The mechanism proposed [82] is for HALS to prevent isomerisation by rapidly donating a hydrogen atom to the photodissociated C - H bond before the hydrogen atom from that bond attatches itself to the $\alpha$ - carbon

atom, i.e. :-




Allen et al [83] also suggest a reaction between $\alpha,\beta$ - unsaturated ketones and nitroxide radicals, along similar lines.

There are, however, several problems with this mechanism, not least of which is the lack of agreement over whether the phosphorescence spectra used to identify the species are in fact caused by $\alpha,\beta$ - unsaturated carbonyls in the first place [2,6], as already noted in Section 1:1. The mechanisms require extremely fast hydrogen transfer, or radical attack by nitroxide, something which might not be possible in a polymer matrix. In the case of tertiary amines, H - transfer is obviously dependent on the conversion of the original material to a secondary amine. Lastly, the basic $\alpha,\beta$ - unsaturated ketone is still left intact, able to absorb and possibly transfer energy, resulting in bond scission and radical formation.

f) Radical Scavenging This aspect of the photostabilising ability of HALS is usually considered in terms of the corresponding nitroxide derivatives which are thought to be efficient alkyl radical traps [84]. This ability is conferred by the existence of free valency localised on the oxygen [85]. Nitroxides can readily dimerise [86], and if $\alpha$- hydrogens are available, then disproportionation may take place. HALS of course contain no $\alpha$- hydrogens, and the effect of the disproportionation reaction can be seen in comparing the superior photostabilising ability of 2,2,6,6-Tetramethylpiperidine with the poorer ability of 2,6-Dimethylpiperidine [56].

The mechanisms whereby the nitroxide radicals are formed from the parent amines, along with subsequent reactions to form other, substituted, products have been described in Section 2:2; but here we will look at the mechanism, and efficiency, of radical scavenging by HALS derivatives in more detail.

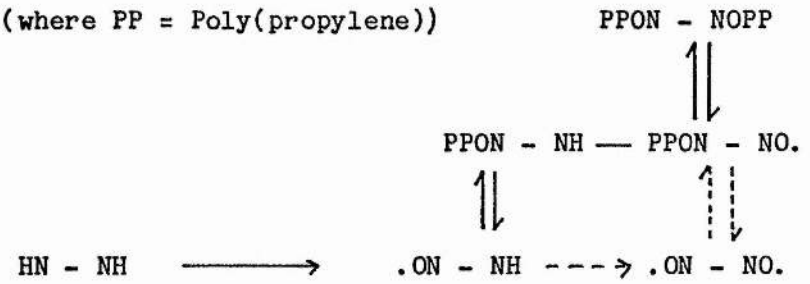
In a comprehensive investigation of poly(propylene) photodegradation and the effect of HALS and derivatives on the process Carlsson et al [87] conclude that only a small fraction of peroxy radicals cause the bulk of the degradation. Most terminate, after only a few propogation steps, with other peroxy radicals descended from the same initiating event. The few that escape this secondary cage recombination produce long - lived species of high kinetic chain length. It is suggested that HALS and their derivatives stabilise poly(propylene) by acting as inefficient scavengers of macroalkyl and macroperoxy radicals. Nitroxide association with oxidised domains is possible [57],

together with decomposition of the grafted substituted hydroxylamine ethers in these oxidised regions [53].

The authors [87] also noted that both the parent HALS and its nitroxide, when initially compounded with separate poly(propylene) samples, are quickly reduced in concentration during photo-oxidation, and concluded that the photstabilisation of a poly(propylene) film containing HALS as additive must occour in the presence of a low residual NO. concentration, and in the presence of the grafted hydroxylamine ether. Work with model systems showed that nitroxides and hydroxylamine ethers can be expected to operate only as very weak radical scavengers, however the authors suggest that this should be enough to markedly affect the low population of high kinetic chain length radicals.

Later work by the same group [88], using the dimeric stabiliser Tinuvin 770, suggested the following reaction sequence :-

(where PP = Poly(propylene))




The mononitroxide will exist in very low concentration compared with the grafted dispecies

Regeneration of nitroxide will proceed via the radical trapping cycle already defined, i.e. :-

$$NO. + PP. \longrightarrow NOPP$$

$$NOPP + PPOO. \longrightarrow NO. + PPOOPP$$

The authors [88] consider that, after a period of photo-oxidation, the hydroxylamine ether will be the predominant stabiliser derived species in a polyolefin matrix. The dependence of the decomposition rate of hydroxylamine ethers on the polarity of the environment implies that NOPP decomposition, and hence scavenging of macroperoxy radicals, should be most rapid in highly oxidised domains within the polymer.

As we have now seen, there is some difference of opinion over the efficiency of nitroxides as radical traps. Some authors [52,89] have tended to conclude that the nitroxide radicals are the only species involved in the photostabilisation mechanism of HALS, but this has been questioned [56] on the grounds that there is only a low percentage of the original HALS present as a steady state population of radicals. As noted already, even combining the scavenging of alkyl radicals by nitroxides, and peroxy radicals by hydroxylamine ethers, cannot explain the excellent photostabilising ability of HALS. Moreover, Allen [90] has shown that the amount of nitroxide radicals formed from HALS is dependent on the hydroperoxide concentration. In a series of experiments on pre-oxidised poly(propylene) samples, it was shown that NO. concentration increased with rising ROOH content, but that the shortest embrittlement times occoured for samples containing the highest concentrations of nitroxide radicals. Even though in all cases the degradation times were higher than that of an unstabilised sample, this indicates that high stability need not be connected with the presence of nitroxide radicals. A similar conclusion may be drawn from the work of Felder et al [64] already mentioned.

Besides the nitroxide radicals and hydroxylamine ethers, the possibility of radical trapping by HALS - derived hydroxylamines has been suggested [62]. The O - H bond dissociation energy of these compounds is quite low [91]. They have been shown [63] to act as peroxy radical scavengers via hydrogen transfer, with a rate constant of c. $5 \times 10^5$ $M^{-1}$ $s^{-1}$, which ranks them among the more powerful chain - breaking antioxidants. The actual steady state concentration of such species would be small. Hydroxylamines may be formed via photolysis of ROOH - HALS associations as shown earlier, or via the thermal dissociation of hydroxylamine ethers [61]. The scheme proposed for this is shown in section 2:2. Reaction scheme B predominates in the presence of oxygen, but it has been suggested [92] that in the polymer matrix reaction A might become important. Chakraborty and Scott [60] have observed a steady buildup of unsaturation during photo-oxidation of HALS stabilised poly(propylene), and attribute this to reaction A.

## 2:4 Overview and Aims

As may be seen from the prceeding section, a large variety of stabilising mechanisms have been attributed to HALS. The interconversion of the basic hindered amine to nitroxide radicals, hydroxylamine ethers, and hydroxylamines, via the destruction of hydroperoxides, peroxy radicals, and alkyl radicals, is now the mechanism which appears to be most favoured, but the low concentrations of these species, and the probable low rates of interconversion may be a drawback. In most cases, experiments have been carried out in fluid solution, and the ability of large molecules such as macroperoxides and HALS to

encounter each other in a rigid polymer matrix is something which must be considered of paramount importance.

In this work we have examined four aspects of the effect of HALS on the photo-oxidation of hydrocarbons.

a) ROOH - HALS Interaction Although direct destruction of hydroperoxide by HALS has been deemed unlikely, the creation of NO., which enables the radical trapping cycle to be set up, has been inextricably linked with the ability of HALS to interact closely with ROOH, and thus be on hand to prevent the initiation of the autoxidation cycle by radicals produced by ROOH photodissociation. Without this association it is difficult to explain the photostabilising ability of low concentrations of HALS in terms of a radical trapping mechanism.

The quoted association constants ($K_A$) of these associations are low, and it was decided to investigate this reaction in order to confirm or refute this situation, and to then calculate the probable level of association present in a photo-oxidising polymer system.

b) Excited State Quenching The ability of HALS and their derivatives, particularly the nitroxide radicals, to quench EES has been investigated by a few authors, but results tend to be difficult to correlate because of the different chromophores and measuring methods used to calculate the efficiency of any quenching reaction. In this investigation we have attempted to overcome this difficulty by investigating a few specific systems to determine the ability of HALS and derivatives to interact with

EES. Investigations included both singlet and triplet manifold processes, and a comparison of the ability of HALS as quenchers of $n - \pi^*$ and $\pi - \pi^*$ excited states, both of which might be present in a polymer, depending on the particular impurity involved. Thus we hoped to produce a comprehensive survey of the EES quenching ability of HALS and their derived nitroxide radicals.

c) Transition Metal Impurities Although it has been shown that transition metal ions are capable of catalysing the photo-oxidation of hydrocarbons, and routine tests on commercial polymers show the presence of numerous transition metal species, little or no work has been undertaken to investigate the possibility of stabiliser species acting as scavengers of these highly active, mobile, species. The fact that amine complexes of transition metals are common would seem to suggest that HALS might be able to operate by this means, thus destroying the hydroperoxide - metal ion complexes which have been suggested as powerful initiators of hydrocarbon photo-oxidation [28].

We thus carried out a series of experiments, using various commercial HALS, and model compounds, to determine the ability of HALS to operate in this way.

d) Diffusion Processes In any photo-oxidising polymer system notice must be taken of the ability of oxygen to diffuse into the system and react with alkyl radical species to propagate the autoxidation cycle. By means of a theoretical model, an attempt was made to determine the importance of this process as a rate determining step in polyolefin photo-oxidation.

Similarly, a stabiliser in a polymer will be able, to a greater or lesser extent, to diffuse through a polymer matrix. Stabilisers are designed to have sufficient molecular weight to prevent their ready diffusion to the surface of a polymer and loss by volatilisation.

Great store is set, by many authors, on the ability of HALS to operate by associating with oxidising domains in a polymer. Since the macrohydroperoxides are attached to the polymer backbone, their mobility is strictly limited, and it would appear that HALS would have to move about in the matrix to encounter such sites. The high M.W. and, in some cases, polymeric nature of commercial HALS make this an aspect of the stabilisers behaviour which requires closer examination. While noting that some of this movement may take place in the melt phase, during processing, even this would be a highly viscous medium, and the type of H - bonded association thought to form may itself be disrupted at elevated temperatures.

In order to assess the consequences of this problem, a short literature survey of the processes involved in stabiliser diffusion was undertaken.

## 3. SYNTHESIS

### 3:1 Origin and Characterisation of Hindered Amines

a) Model Compounds The model compounds used during this investigation were - 2,2,6,6 - Tetramethylpiperidine, 4 - Amino - 2,2,6,6 - tetramethylpiperidine, and 2,2,6,6 - Tetramethylpiperidine - N - oxyl free radical. All were obtained from Aldrich Chemical Company Ltd., and were used as supplied.

b) Commercial HALS All the HALS used in this study were manufactured by Ciba - Giegy Ltd.. Samples were supplied by Dr. T.J. Henman, and by the manufacturers. Structures of some of those used are shown in Figure 2.1.

Analyses of samples, and relevent data, are given below :-

I. Tinuvin 770 $C_{28}H_{52}O_4N_2$

| | Theoretical(%) | Actual(%) |
|---|---|---|
| C | 69.96 | 69.89 |
| H | 10.90 | 11.37 |
| O | 13.31 | 13.02 |
| N | 5.83 | 5.72 |

UV/Visible absorption spectroscopic analysis of the stabiliser showed no appreciable absorbance above 250nm ($10^{-4}$M in $CH_2Cl_2$; 1cm cell.). The material is a white powder, readily soluble in most organic solvents. T770 is commercially produced Bis(2,2,6,6 - tetramethylpiperidine) sebacate.

II. Tinuvin 292 $C_{30}H_{56}N_2O_4$

| | Theoretical(%) | Actual(%) |
|---|---|---|
| C | 70.82 | 70.80 |
| H | 11.09 | 10.93 |
| O | 12.58 | 12.72 |
| N | 5.51 | 5.49 |

UV/Visible absorption spectroscopic analysis of the stabiliser showed no appreciable absorption above 250nm ($10^{-4}$M in $CH_2Cl_2$; 1cm cell.). This material is a yellowish liquid, soluble in most organic solvents; it is Bis(1,2,2,6,6 - pentamethylpiperidine) sebacate, and can therefore be regarded as a tertiary analogue of Tinuvin 770.

III. Tinuvin 622 $(C_{15}H_{25}O_4N)_n$

| | Theoretical(%) | Actual(%) |
|---|---|---|
| C | 63.58 | 63.53 |
| H | 8.89 | 9.05 |
| O | 22.59 | 22.52 |
| N | 4.94 | 4.90 |

UV/Visible absorption analysis of this stabiliser showed no appreciable absorption above 250nm ($10^{-4}$M in $CH_2Cl_2$; 1cm cell.). This particular material is a granular white solid; due to its tertiary, polymeric, nature it is slowly soluble in chlorinated hydrocarbons, but sparingly soluble in hydrocarbons and alcohols.

IV. Chimassorb 944 $(C_{35}H_{66}N_8)_n$

| | Theoretical(%) | Actual(%) |
|---|---|---|
| C | 70.19 | 69.94 |
| H | 11.11 | 11.18 |
| N | 18.71 | 18.88 |

UV/Visible absorption spectroscopic analysis of this stabiliser showed there to be, unlike the others, a substantial absorbance at 250nm, tailing off to a negligible level at c.270nm. This is most likely due to the quasi - aromatic triazine ring in the backbone of the polymer. The material is an off - white powder, soluble in most organic solvents.

The effect of the increased absorbance of C944 is graphically illustrated when samples of poly(propylene) stabilised by the various HALS are subjected to unfiltered light from a medium pressure Hg lamp. It was found that C944 offered no protection against photo-oxidation under such actinic light; in fact it appeared to act as a sensitiser at later stages of the reaction. All other HALS substantially increased the lifetime of poly(propylene) under these circumstances.

## 3:2 Synthesis of HALS and Nitroxides

### a) 4 - Methacryloylamino - 2,2,6,6 - tetramethylpiperidine

It was decided to synthesise this particular hindered amine as it offered possibilities for homo-, and co-polymerisation to provide alternative, better characterised, polymeric HALS. The method used was based on that of Kurosaki et al [93].

To a mixture of 10g 4 - amino - 2,2,6,6 - tetramethylpiperidine and 8g triethylamine in 170ml dry benzene, was added 7.1g of methacryloyl chloride, with stirring, under cooling in a water ice bath to 5 - 10°C. The reaction was allowed to reach RT over a period of approx. 1hr, and then left at RT for 20hrs. The precipitate of a complex of product with triethylamine hydrochloride was filtered out of the reaction mixture, and dissolved in a saturated aqueous solution of $K_2CO_3$. The resulting solution was extracted with 500ml $CHCl_3$, and this solvent removed gently under vacuum. The crude product was recrystallised twice from cyclohexane, giving a white, semi-crystalline, product. M.p. = 123 - 125°C (literature value = 126°C); Yield = 70%.

In order to assess the differences in behaviour between a monomer and its respective polymer, it was decided to polmerise a sample of this material. A solution of 1.0g of monomer and 2mg azobisisobutyronitrile (AIBN) in 5ml benzene was placed in a 20ml ampoule fitted with a tap, and the mixture degassed by means of a series of freeze/pump/ thaw cycles on a vacuum line. The sample was then polymerised by heating in a water bath at 70° C for 24hrs. The polymeric product was precipitated by addition of the reaction mixture to ether, and purified by repetition of this proceedure. The final product was dried in a vacuum oven at RT for 5 days.

b) Nitroxide Radicals Various methods for the conversion of secondary amines to nitroxide radicals have been proposed, but the most successful to date was first put forward by Chapelet-Letourneux et al [94]. This involves oxidation of the amine by two equivalents of a peracid, the reaction producing first a hydroxylamine, and then the nitroxide radical. Keana et al [95] used this method for the synthesis of spin labels, while later Toda et al [96], and Rauchman et al [97], refined the method to give high yields of the radical, using m-chloroperbenzoic acid as the oxidant. We have used the methods of both Toda and Rauchman, which differ only in detail, modified to account for the multifunctionality of the HALS under consideration. The m-chloroperbenzoic acid (mCPBA) used was 85% pure and was supplied by Aldrich.

A solution of $10^{-3}$ moles Tinuvin 770 in 50ml $CH_2Cl_2$ was stirred for 15 minutes in an ice water bath. A solution of $4 \times 10^{-3}$ moles mCPBA in 50ml $CH_2Cl_2$ was added dropwise over a period of 30min with vigo rous stirring, the resultant solution being removed from the bath and allowed to stand at RT for 6hrs. The red solution was washed three times with 5% $Na_2CO_3$ solution to remove acid product, and dried over $MgSO_4$ overnight. The solution was filtered into a Buchi flask and the solvent removed under vacuum. The crude product was recrystallised twice from methanol. Yield 80% M.p.98 - 100° C (Lit. 101° C). Microanalysis :- Calculated - C65.85, H9.87, O18.80, N5.49, Actual - C65.99, H9.87, O18.70, N5.44.

The nitroxide of Chimassorb 944 was prepared in a similar manner. Yield c.50% M.p. - Sample commenced melting at 151°C, decomposition occoured by 200°C. Microanalysis :- Calculated - C66.84, H10.26, O5.09, N17.82, Actual - C65.90, H10.31, O5.93, N17.86. The high oxygen content may be due to oxidation of the unhindered secondary amine group in some of the monomer units of the stabiliser.

In the case of Tinuvin 622, a tertiary amine, reaction with a peracid would be expected to produce an amine oxide. Carrying out the above proceedure gave a yellowish tar-like substance. Even using the improved tertiary amine N - oxide proceedure of Craig and Purushothman [98] only a tarry, hygroscopic, product could be obtained. Attempts to isolate an amine N - oxide were then abandoned. No synthetic pathway could be found at this stage for the direct conversion of a tertiary amine to a nitroxide radical.

Similarly no attempt was made to oxidise the other tertiary amine, Tinuvin 292.

# 4. EXPERIMENTAL AND RESULTS

## 4:1 Interaction of HALS with Excited State Species.

### 4:1:1 Singlet State Interactions

#### a) Polynuclear Aromatics - Effect of HALS on oxidation

Polynuclear aromatic compounds (PNA), such as anthracene and tetracene, are readily oxidised under photo-oxidising conditions [99,100,101] to produce transannular peroxides, which in turn react to produce a variety of quinoid type compounds and radical breakdown species. Under inert conditions, or in cases of severe oxygen depletion, these compounds form dimers [102] with effective breakup of conjugation and hence reduced absorption in the visible region of the spectrum. It was thought that HALS derivatives, particularly the stable nitroxide radicals, might in some way affect this process, either by scavenging of alkyl radicals, or by quenching of singlet oxygen, suspected to be responsible for the oxidation, as suggested by Bellus et al [67]. Experiments were carried out both in fluid solution and in polymer matrix, to investigate the effect of nitroxide radicals derived from HALS on the oxidation of PNA compounds.

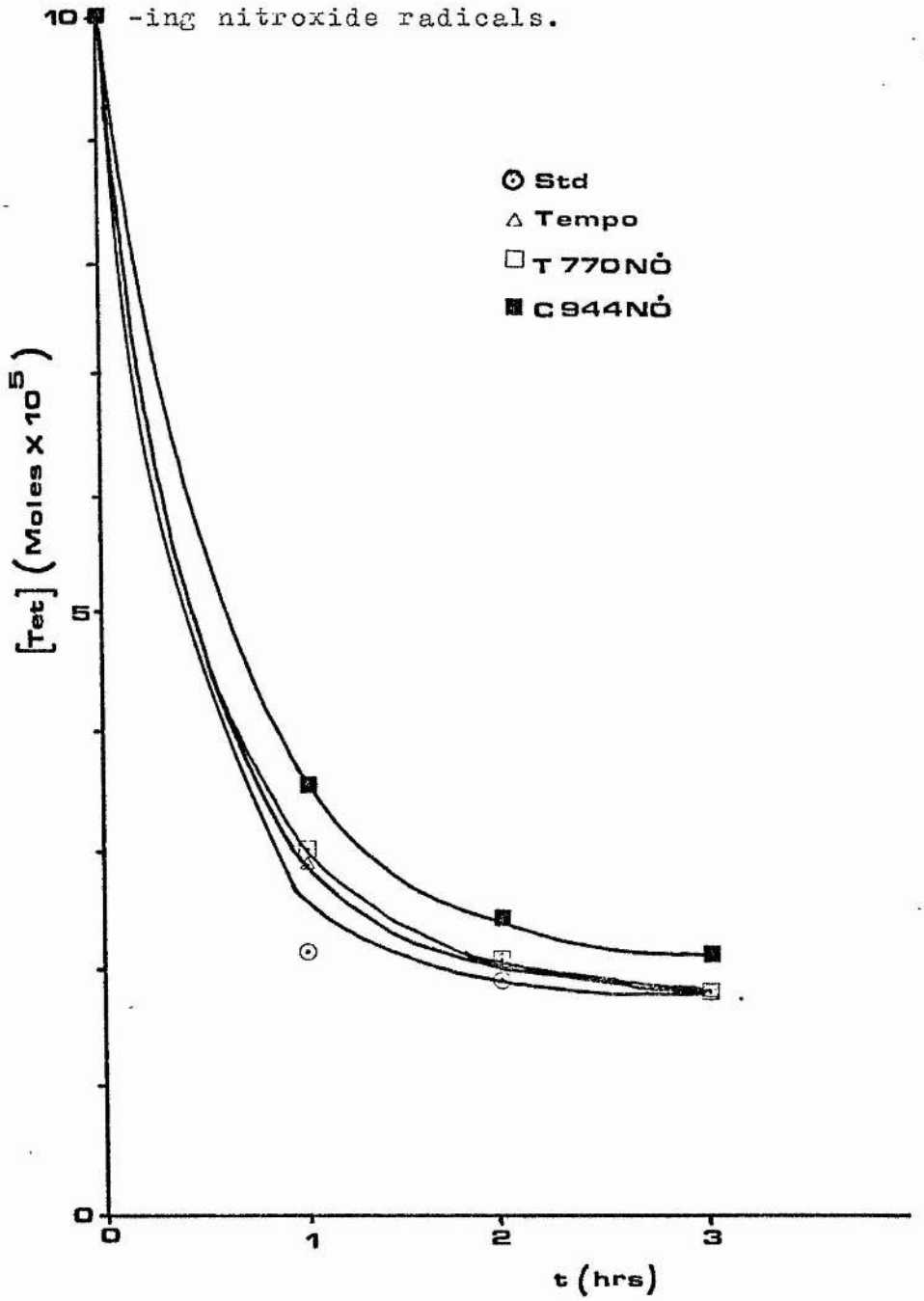
1) Tetracene in Fluid Solution Tetracene was purified by twice recrystallising from ethanol, and drying in a vacuum oven at 30 $^{o}$C for 3 days. The nitroxides used were prepared as described in Chapter 3. Methylene chloride was dried over calcium chloride and distilled immediately prior to use.

Tetracene solutions fade rapidly in the presence of light and $O_2$ and great care had to be taken to prevent deterioration of experimental solutions prior to use. This was achieved using nitrogen flushed solvents, and excluding light during sample preparation. Equimolar amounts of tetracene and each of the radicals ($10^{-4}$ mol $dm^{-3}$) were used, and samples exposed to diffuse sunlight in the laboratory. Disappearance of the characteristic absorbance bands due to tetracene was followed using a Unicam SP800 UV/Visible Spectrophotometer, and any effects on the emission spectroscopic characteristics of the solutions were followed using a Perkin - Elmer MPF - 2A Spectrofluorimeter.

On exposing the sample solutions to light, they rapidly faded. After only 2hrs, the low energy absorptions of tetracene between 350 and 500nm had almost entirely disappeared. However, absorption spectra showed that the presence of the radical additives was inhibiting the reaction (Figure 4.1); the efficiency of this inhibition can in fact be seen to proceed in the order TEMPO T770NO. C944NO., with the last being consiserably more efficient than the other two. Emission spectroscopy shows this up even more graphically; going from the standard sample through TEMPO, T770NO., and C944NO. the spectra show an increasing tendency to retain the characteristic features of the tetracene fluorescence [103] under photo-oxidising conditions.

Figure 4.1

Disappearance of Tetracene under photo-oxidation conditions in methylene chloride samples contain -ing nitroxide radicals.



In order to confirm that this is a genuine effect of HALS nitroxides on the photo-oxidation of PNA, the experiments were repeated using phenanthrene, which is non - oxidisable under our experimental conditions. No change was noted in the absorption or emission spectra of any of the samples, even after 40hrs exposure to light.

The absorption and emission characteristics of $CH_2Cl_2$ solutions of tetracene with the parent HALS were investigated. No marked differences were noted between the samples in the rates of peak disappearance. This seems to suggest that the reaction is exclusive to the radical species.

2) Anthracene in Poly(methylmethacrylate) Matrix PMMA was a commercial sample (RAPRA) and was purified by two cycles of dissolution and precipitation. Product was dried in a vacuum oven at 30°C for 2 days, and stored in the dark. Anthracene was Aldrich "Gold Label" material (99.99+% pure), and was used as supplied. $CH_2Cl_2$ was purified by drying with $CaCl_2$ and fractionally distilling. TEMPO (Aldrich) was used as supplied. T770NO., and C944NO., were prepared as shown in Chapter 3.

A $10^{-2}$ mol $dm^{-3}$ solution of PMMA was made up in $CH_2Cl_2$, and $10^{-2}$ M anthracene (w.r.t. PMMA) added. Solvent was deoxygenated by purging with oxygen - free nitrogen for 5min., and this master batch stored in the dark. 5ml volumetric flasks were charged with $10^{-3}$M (w.r.t. PMMA) of the necessary radical, and made up to volume with the master solution. Films were cast onto 25mm quartz disks to a thickness of 0.055 + 0.002mm, removed from the

Figure 4.2

Diagram of apparatus for photolysis of polymer films.

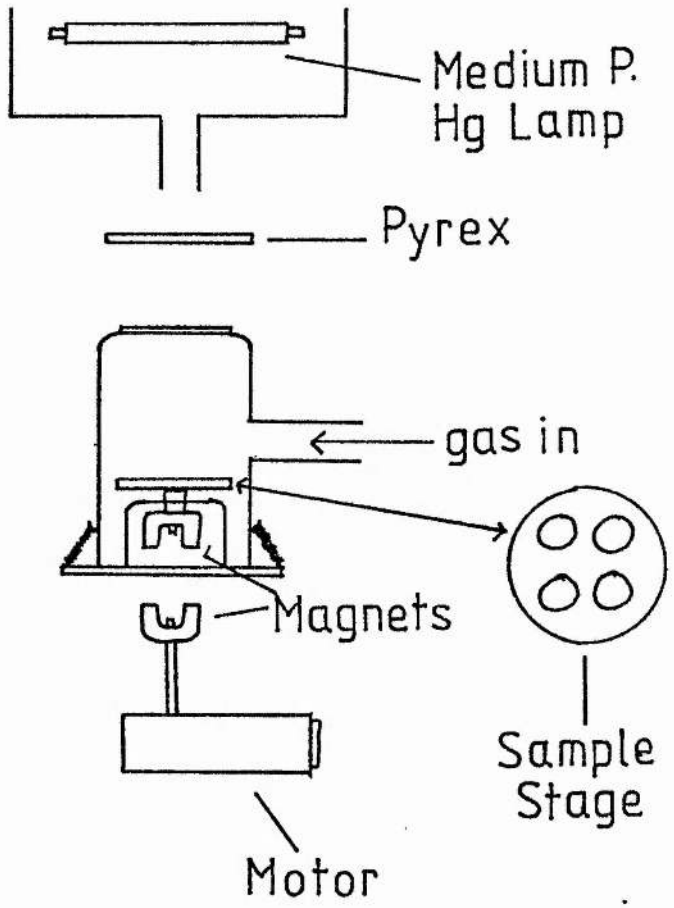


Figure 4.3

Disappearance of Anthracene under photo-oxidation conditions in PMMA matrix containing nitroxide radicals - Air atmosphere.

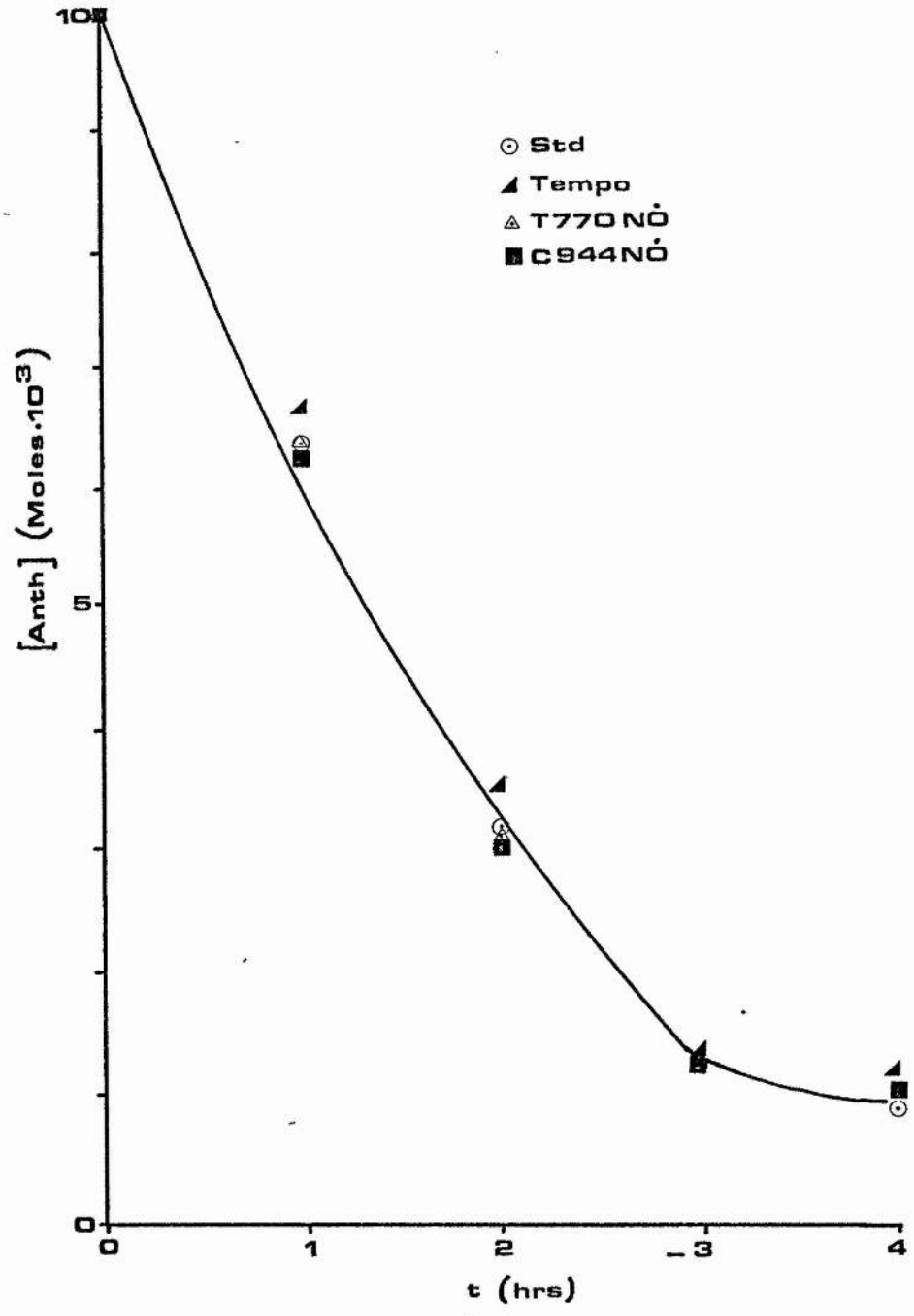
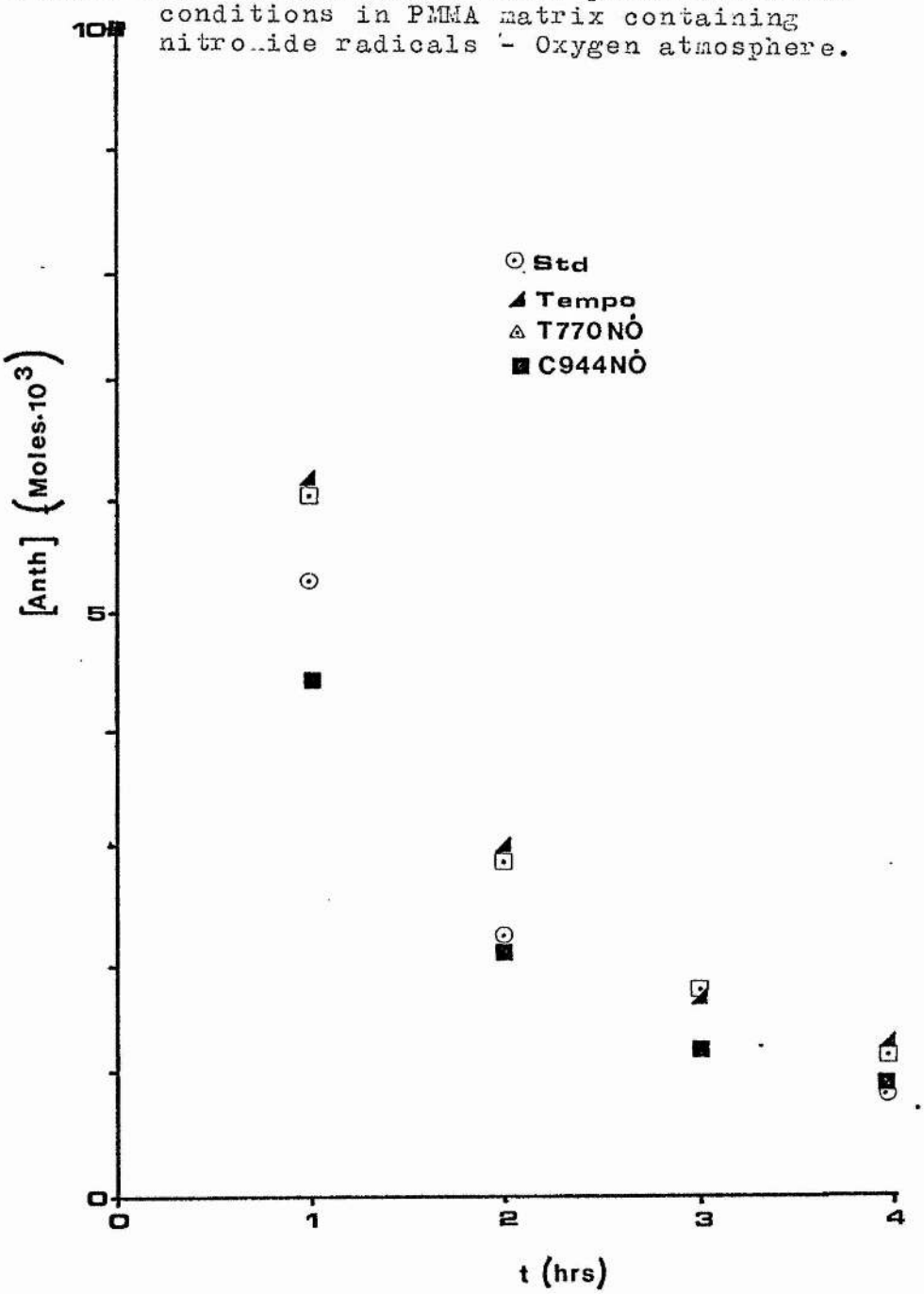


Figure 4.4

Disappearance of Anthracene under photo-oxidation conditions in PMMA matrix containing nitro..ide radicals - Oxygen atmosphere.



disks after 1hr, and dried in a vacuum oven at RT for 2 days. Films were stored in the dark until required.

The apparatus used for the photo-oxidation of these samples is shown in Figure 4.2. This set-up allows the simultaneous irradiation of a standard sample plus three test samples. The slow rotation of the stage evens out any discrepencies in the transmittance of the filter. Two series of experiments were carried out in this apparatus; one using air, and the other using a pure oxygen atmosphere.

The disappearance of the characteristic anthracene absorption was used as a measure of the extent of the reaction. The particular peak used was the 377.5nm absorption, this being furthest away from any possible interference due to additive or product absorbances, and nearest to the 0 - 0 electronic transition. The data was plotted as shown in Figures 4.3 and 4.4.

It is not possible, unfortunately , to differentiate between product due to oxidation and that due to dimerisation, therefore any effect found on addition of nitroxides will not necessarily be due to singlet oxygen quenching, but this is the most likely effect since radical formation at the 9 and 10 positions of anthracene does not appear to happen [100].

b) Naphthalene - Stern-Volmer Kinetics.

Aliphatic amines will, almost invariably, have excited state levels of much higher energies than those associated with PNA compounds, and so would not be expected to quench PNA fluorescence by long range transfer. Close encounter energy transfer has been proposed to occ ur between amines and excited molecules through formation of an excited charge transfer (CT) complex, or exciplex [104]. Tertiary amines [105] have been shown to be moderately efficient EES quenchers, while more recent work has suggested that these complexes are highly ionic in character [106], and that the interaction can be highly complex, involving triplet species in some cases [107].

The ability of a comprehensive series of amines to quench the singlet EES of naphthalene was investigated using Stern - Volmer kinetics. This technique may be described as follows :-

Consider quenching of the emission of an excited molecule $D^*$ by the addition of a second molecule A. Assume the following mechanism for formation and disappearance of $D^*$ -

| | | |
|---|---|---|
| Absorption | $D + h\upsilon \longrightarrow D^*$ | Ia |
| Emission | $D^* \longrightarrow D + h\upsilon'$ | $k_1 [D^*]$ |
| Quenching | $D^* + A \rightarrow A^* + D$ | $k_2 [D^*][A]$ |
| Deactivation | $D^* \longrightarrow D + \text{heat}$ | $k_3 [D^*]$ |

Under conditions of steady illumination, and no irreversible photochemical reactions, we have

$$d[D^*]_{/dt} = Ia - (k_1 + k_2[A] + k_3)\,[D^*]$$

The quantum yield for $D^*$ emission in this case is :-

$$\phi_A = k_1[D^*]_{/Ia} = k_1/k_1+k_3+k_2[A]$$

TABLE 4.A

Table of results of Stern - Volmer kinetic investigation of the interaction of amines with naphthalene.

| Compound | $k_Q$ ($M^{-1}$ $s^{-1}$ $10^7$) |
|---|---|
| DABCO | 505 |
| Chimassorb 944 | 422 |
| 4-Methacryloyl-2,2,6,6 TMP | 239 |
| 1,2,2,6,6-PMP | 158 |
| Triethylamine | 46 |
| Tetramethylethanediamine | 42 |
| Di-n-butylamine | 28 |
| 2,2,6,6-TMP | 26 |
| Piperidine | 23 |
| Poly(4-MA-2,2,6,6-TMP) | 23 |
| Pyrrolidine | 22 |
| Morpholine | 20 |
| 4-Amino-2,2,6,6-TMP | 15 |
| Tinuvin 770 | 15 |
| N-Methylmorpholine | 9 |
| Cyclohexylamine | 7 |
| Hexamine | neg. |
| Tinuvin 622 | neg. |

Dividing the above into the quantum yield expression for $D^*$ alone we obtain the Stern - Volmer relationship:-

$$\phi_0/\phi_A = 1 + k_2\tau[A] \quad , \quad \tau = \text{measured lifetime}$$

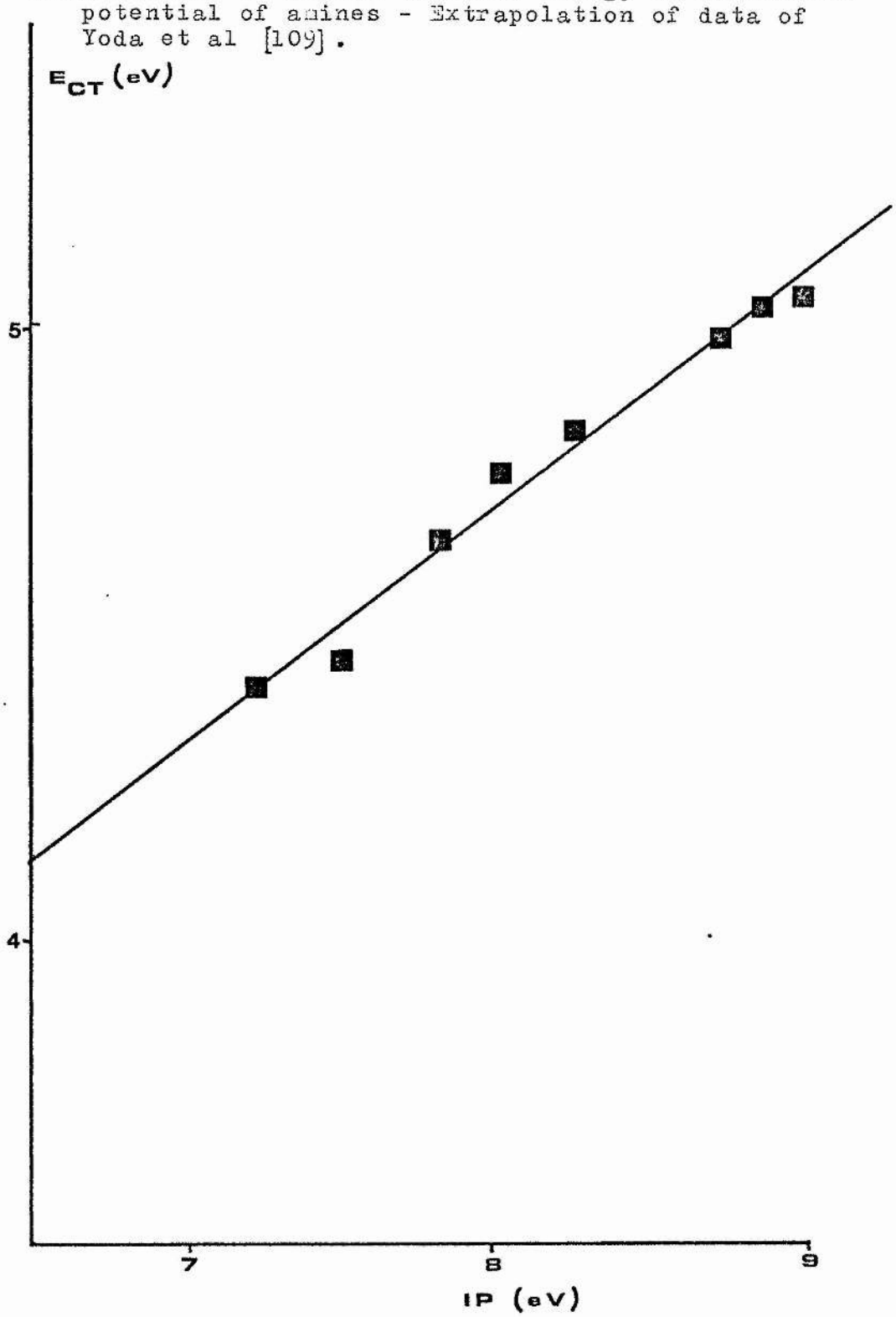
If we now plot $\phi_0/\phi_A$ vs [A] we obtain a straight line with a slope of $k_2\tau$. Since $\tau$ can be obtained, the bimolecular quenching constant for deactivation of a particular EES by a particular amine can be derived.

The experimental $k_2$ values of the various amines were obtained in the following manner. Solutions of fixed concentration of naphthalene ($10^{-3}$ mol $dm^{-3}$) and varying concentrations of amine ($5 \cdot 10^{-4}$ mol $dm^{-3}$ - $5 \cdot 10^{-3}$ mol $dm^{-3}$) in $CH_2Cl_2$ were subjected to emission spectroscopic analysis in a Perkin - Elmer MPF-2A Spectrofluorimeter. Since the intensity of fluorescence of a sample is proportional to its quantum yield, the ratio of initial intensity to intensity at each additive concentration was plotted against [A] to obtain a straight line of slope $k_2\tau$. Using a linear regression programme the values of $k_2\tau$ were obtained. Taking the value of $\tau$ for naphthalene to be $10^{-7}$s, the values for $k_2$ for each of the amines was obtained. These values are shown in Table 4A.

Heller and Blattman [31] have suggested that, for a given sensitiser in a given solvent, the quenching rate constant of an amine would be proportional to its ionization potential (IP). They found that this held for non-hindered and tertiary hindered amines but that secondary hindered amines did not share the same relationship and were much weaker quenchers than would be expected from their IP's. The authors vague suggestion that this

Figure 4.5

Relationship of charge transfer energy to ionisation potential of amines - Extrapolation of data of Yoda et al [109].



is due to steric effects is not very satisfactory in view of the results for tertiary hindered amines, and we decided to treat our $k_Q$ data in a similar manner to ascertain what relationship held between the quenching efficiency and IP of an amine. Yoda et al [109] have shown there to be a direct relationship between the energy of CT bands exhibited by amine complexes, and the IP of these amines. Using Iodine as an electron acceptor, the wavelengths of amine - $I_2$ CT bands were obtained using a Perkin - Elmer SP8-100 Spectrophotometer, and the band energies calculated. Values of the IP's were obtained by correlating these CT energy values to an extrapolated plot or $E_{CT}$ vs IP obtained from the data of Yoda et al [109]. (Figure 4.5)

Plotting $k_Q$ vs IP for the series of amines used, we obtained the result shown in Figure 4.6.

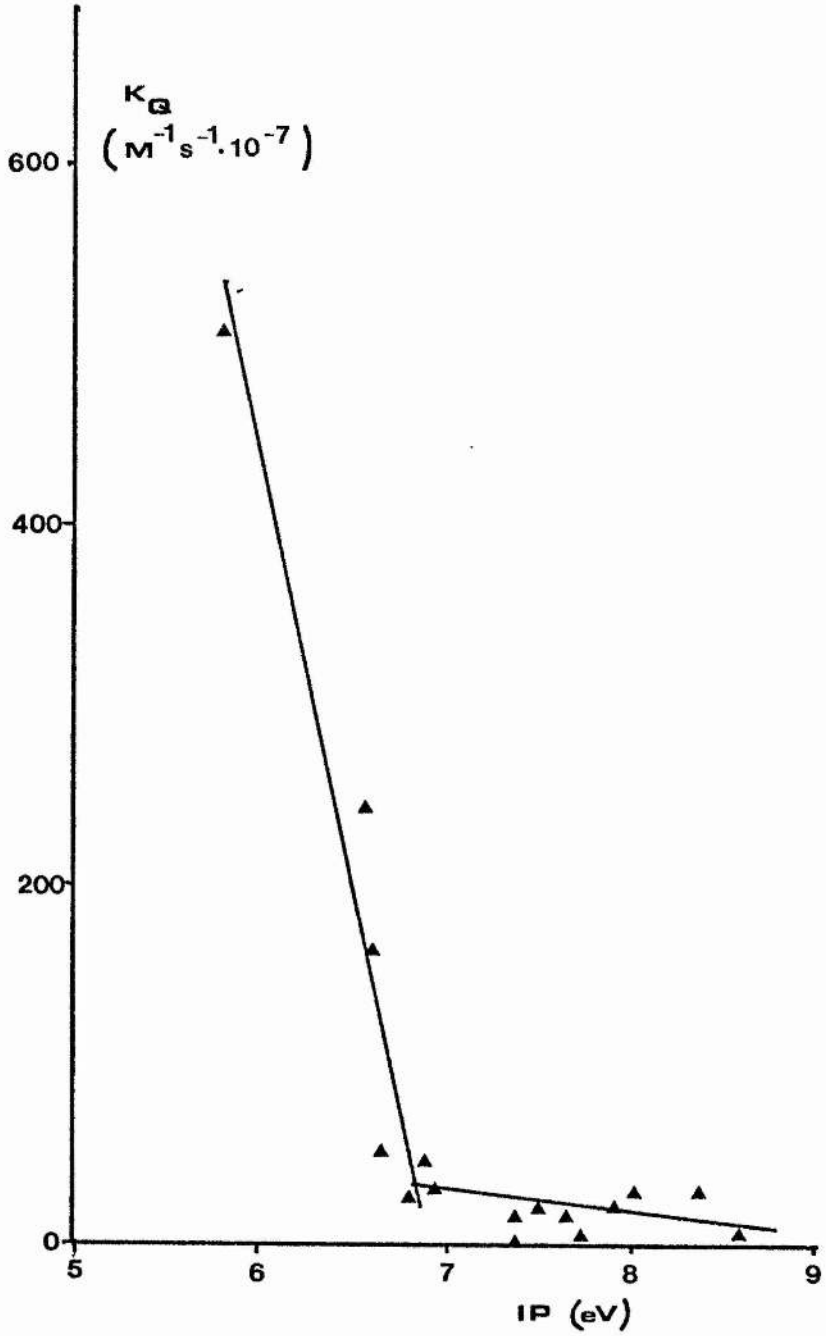
Similar investigations to the above were attempted for the nitroxide radicals, but this was not found to be possible for two reasons 1) The highly coloured radicals interfere with emission spectroscopy and hence the $k_Q$ values obtained are unreliable, and 2) nitroxides do not form CT complexes with iodine.

c) Discussion

Our results show there to be a small, but non-negligible, effect of nitroxides on the oxidation of PNA compounds. Since nitroxide radicals have been shown to be quenchers of singlet oxygen [67] it is reasonable to assume that it is by this pathway that the antioxidant properties of the HALS nitroxides are obtained, in this case. However, any effect on polymer stability by this method would be negligible, even supposing the presence

Figure 4.6

Relationship between quenching coefficient and ionisation potential for amines.



of a substantial concentration of PNA impurities.

The ability of HALS to quench singlet excited states presents a more interesting picture. All the hindered amines investigated, with the exception of C944 which is a special case due to the pseudo-aromatic triazine ring, are poor quenchers of excited singlets. Figure 4.6 does not, however, show agreement with the findings of Heller and Blattman [31]. Contrary to the results of these authors, we can find no appreciable differance in the behaviour of hindered and non-hindered species, and it can clearly be seen that there is a discontinuity in the relationship between $k_Q$ and IP; when the IP of the amine is above c.6.8eV the quenching ability is negligible, below this value $k_Q$ increases rapidly.

Considering these observations, and taking into account the likely concentrations of the various HALS derivitives and PNA impurities, it must be concluded that quenching of singlet EES, either singlet oxygen or excited chromophores, is not likely to be an important factor in the stabilisation mechanism of HALS.

## 4:1:2 Triplet Interactions

### a) Definition of Experiment

In this section we investigated the effect of addition of HALS on the phosphorescence lifetime of two well characterised triplet levels; that of triphenylene, which results from a $\pi - \pi^*$ electronic transition, and of benzophenone, which results from an $n - \pi^*$ transition. The concept of EES lifetime may be described as follows. If an excited molecular species decays by a unimolecular process with a rate constant $k_x$, the rate of decay

may be written as :-

$$-d[A^*]_{/dt} = k_x [A^*]$$

Integrate $[A^*] = [A_0^*]\, e^{-k\, t}$

$$\ln[A^*] = \ln[A_0^*] - k_x t$$

Hence the value of $k_x$ can be obtained from the resulting straight line and the mode of decay is termed exponential.

By definition [110], the total rate parameter $k_x$ is the sum of all the unimolecular processes, other than dissociative, operating on an excited state. This leads to a definition of an emission lifetime $\tau$, which is equal to the inverse sum of all the rate parameters which deactivate the excited state. For a triplet lifetime this will simplify to the reciprocal of all triplet decay processes. It must be noted here that, in practice, exponential behaviour, and hence a valid value of $\tau$, are only obtained for most molecules at low T, therefore experiments are carried out in liquid nitrogen (77K).

In electronic spectroscopy the luminescence emission intensity is used to follow the course of the decay and if the system obeys the above scheme it can be deduced that a plot of ln intensity against time ought to be linear with a gradient of $-k_T$, therefore the phosphorescence lifetime of the sample can be simply calculated.

Any quenching process, or enhancement of non-radiative decay processes, brought about by addition of HALS or nitroxide will change the sum of the triplet decay processes, and hence lower the lifetime of the system noted from experiment.

b) Triphenylene in Polymer Matrix - $\pi - \pi^*$ Triplets

Due to the relatively long phosphorescence lifetime of triphenylene (c.15s) it was possible to measure the triplet decay of sample films using a Perkin - Elmer MPF-2A Spectrofluorimeter. The output of the spectrofluorimeter photomultiplier was transferred using a Solartron data transfer unit to a Facit 4070 paper tape punch. The triplet decay was monitored using a sampling rate of 1s. The excitation source was a 150 Watt xenon lamp, allowing continuous sample excitation. After establishing a steady state concentration of triplet species, the excitation shutter was closed whilst simultaneously switching on the data transfer unit to sample the voltage decay at predetermined intervals, this generally being followed until three or four first-order lifetimes had elapsed. Results were plotted as ln intensity vs time, and the gradient calculated using a linear regression programme.

Films of PMMA containing $10^{-4}$M triphenylene and $10^{-3}$M of the appropriate HALS or nitroxide were cast from $CH_2Cl_2$ solution to a thickness of 0.050 + 0.002mm, and dried in the dark in a vacuum oven at 25$^{o}$C for 3 days. Samples were placed in a specially constructed quartz cell attached to a vacuum line and pumped down to better than $10^{-4}$Torr. The sample compartment of the spectrofluorimeter was modified to hold a quartz dewer flask, and the sample was cooled in this to 77K during measurements of the triplet decay.

TABLE 4.B

Triplet lifetime of triphenylene in the presence of HALS

| Sample | p (s) |
|---|---|
| Triphenylene, no additive | 14.4 |
| Tinuvin 770, as additive | 14.7 |
| Tinuvin 622, as additive | 14.5 |
| Chimassorb 944, as additive | 14.7 |

TABLE 4.C

Triplet lifetime of triphenylene in the presence of nitroxides

| Sample | p (s) |
|---|---|
| Triphenylene, no additive | 14.4 |
| TMPO as additive | 13.7 |
| T770NO. as additive | 13.4 |
| C944NO. as additive | 13.7 |

Results of the effect of HALS and their nitroxides on the triplet lifetime of triphenylene are shown in Tables 4.B and 4.C. Results are averages of four experimental runs, and all have correlation coefficients better than 0.998.

c) Benzophenone in Polymer Matrix - $n-\pi^*$ Triplets.

Due to the short triplet lifetime of benzophenone ( 5ms) it was not possible to use a simple modification of the spectrofluorimeter as above, and instead a completely new pulsed laser excitation apparatus was required. The principal components of this apparatus were a nitrogen laser excitation source (Lambda Physik K600; 337.1nm line) and a transient recorder for data acquisition (Datalab DL920), the range of which allowed decay events of 0.1ms - 8s to be studied. The versatility of the equipment was further enhanced by interfacing the transient recorder to a microcomputer, thereby enabling the entire data acquisition cycle and subsequent manipulation to be under computer control. A schematic representation of the experimental set-up is shown in Figure 4.7

PMMA films containing $10^{-3}$M benzophenone and various concentrations of Tinuvin 770 or its nitroxide were cast from $CH_2Cl_2$ solution to a thickness of 0.052 + 0.002mm and dried in the manner described above. The sample films were placed in a special cell which was then pumped down to better than $10^{-4}$Torr on a vacuum line, before being transferred to a quartz dewar of liquid nitrogen in the sample chamber of the apparatus. The sample was excited by the laser, and the emission at 450nm was observed.

Figure 4.7

Schematic diagram of pulsed laser lifetime measuring apparatus.

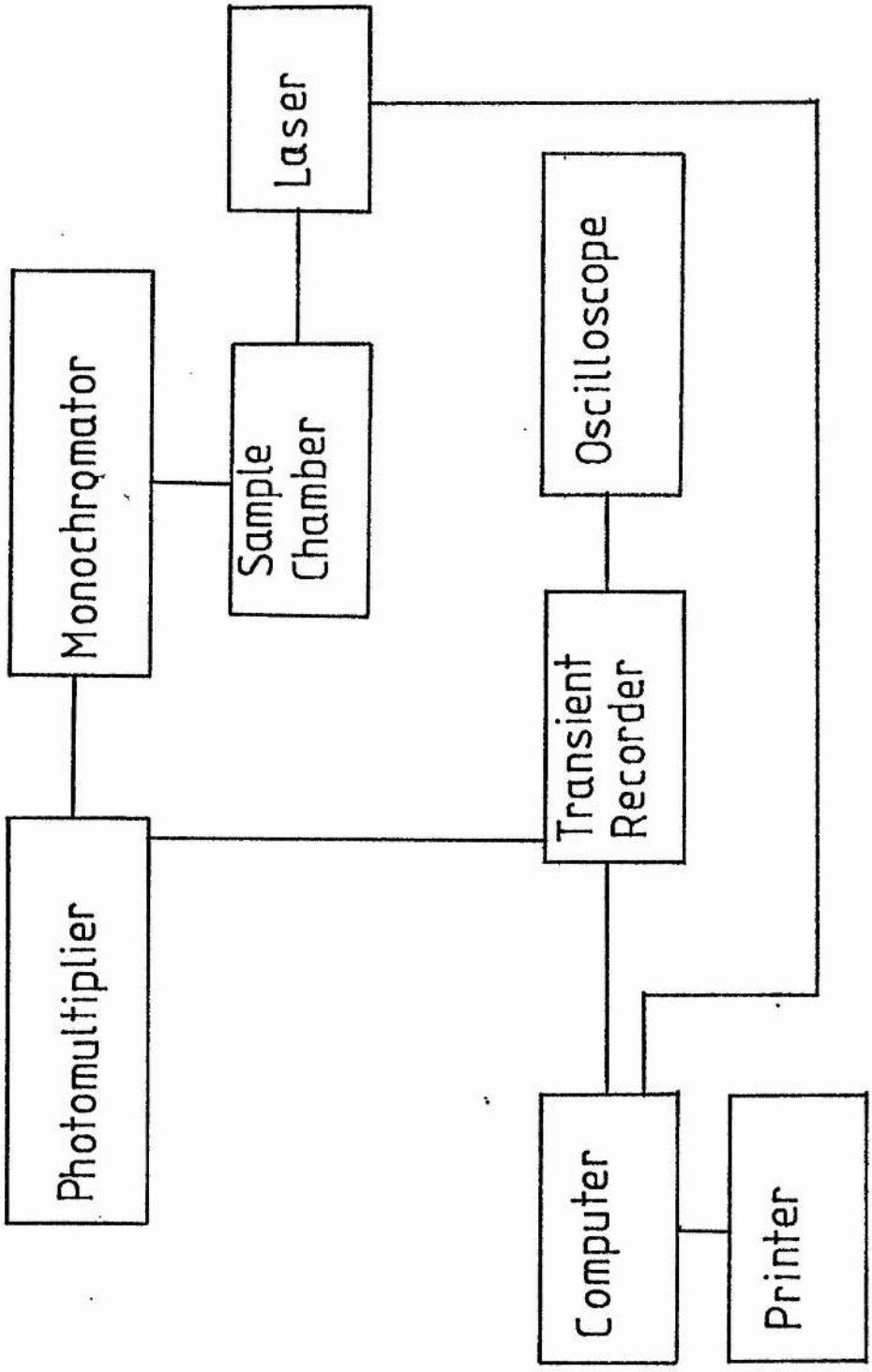


TABLE 4.D

Triplet lifetime of benzophenone in the presence of Tinuvin 770.

| T770 (M) | p (ms) |
|---|---|
| 0 | 4.85 |
| $10^{-4}$ | 4.81 |
| 5 $10^{-4}$ | 4.84 |
| $10^{-3}$ | 4.83 |

TABLE 4.E

Triplet lifetime of benzophenone in the presence of T770NO..

| T770NO. (M) | p (ms) |
|---|---|
| 0 | 4.85 |
| $10^{-4}$ | 4.72 |
| 5 $10^{-4}$ | 4.67 |
| $10^{-3}$ | 4.49 |

Results are shown in Tables 4.D and 4.E; all readings are the average of three runs, and the correlation coefficients are all better than 0.998. Calculations were achieved using the preprogrammed microcomputer [111].

d) Discussion

From the results shown, it is quite clear that HALS, and their nitroxide derivatives, have no appreciable effect on the triplet lifetime of either triphenylene or benzophenone.

4:1:3 Conclusions

Having studied the interaction of HALS and nitroxides with a more extensive selection of excited state species the following observation can be made :-

HALS themselves show no ability to interact with singlet oxygen or with triplet states, and a very poor quenching ability in the case of excited singlets, except for the anomalous Chimassorb 944. This is a moderately good quencher, due most probably to its quasi- aromatic system, and not to the CT interaction undergone by other amines [104], but this also provides a disadvantage in the form of sensitisation under high energy irradiation, and the molecule may itself photofragment to give deleterious by - products.

The ability of nitroxides to quench singlet oxygen and excited singlets has already been established [31], but it is difficult to assess quantitativly by our methods due to the high colour of these species. In any case the low steady state

concentration of these species in a photo-oxidising polymer domain is unlikely to provide a major contribution to stability. An extremely weak ability to quench triplets is exhibited, but is definitely not strong enough to be important in a commercial situation.

## 4:2 Interaction of HALS and Hydroperoxides

We have already noted that hydroperoxides are important intermediates in the autoxidation of hydrocarbons, and it is still proposed that ROOH is the prime photoinitiator in the photo-oxidation of polyolefins [2]. In order to prevent the continuing oxidation reaction, it would be necessary for an additive acting on ROOH to either stabilise the molecule in some way so as to prevent bond scission, or to actively encourage the breakdown but in some way to produce non-radical derivatives.

Because of the low concentrations present in a commercial polymer of both HALS and ROOH, it is necessary that they are in close proximity to each other, if any reaction between them is to have any significant effect on the overall photo-oxidation reaction. This is the reasoning behind the well accepted view that, because of the high basicity of HALS, they are capable of associating with ROOH [55] and thereby either preventing ROOH bond scission, or reacting stoichiometrically to produce the nitroxide radical derivatives.

The validity of such a mechanism depends entirely on the ability of HALS to associate with a high proportion of the available ROOH in a polymer. In this section we used various spectroscopic techniques to investigate the interaction of HALS and ROOH, and to evaluate the importance of such reactions.

### 4:2:1 Nuclear Magnetic Resonance.

In dilute solution (0.05 - 0.5 mol $dm^{-3}$) in $CCl_4$ and $CDCl_3$, the chemical shifts of protons of OH, NH, and SH groups exhibit a substantial concentration and temperature effect on hydrogen

Figure 4.8

Change in NMR chemical shift of hydroperoxy proton with hydroperoxide concentration.

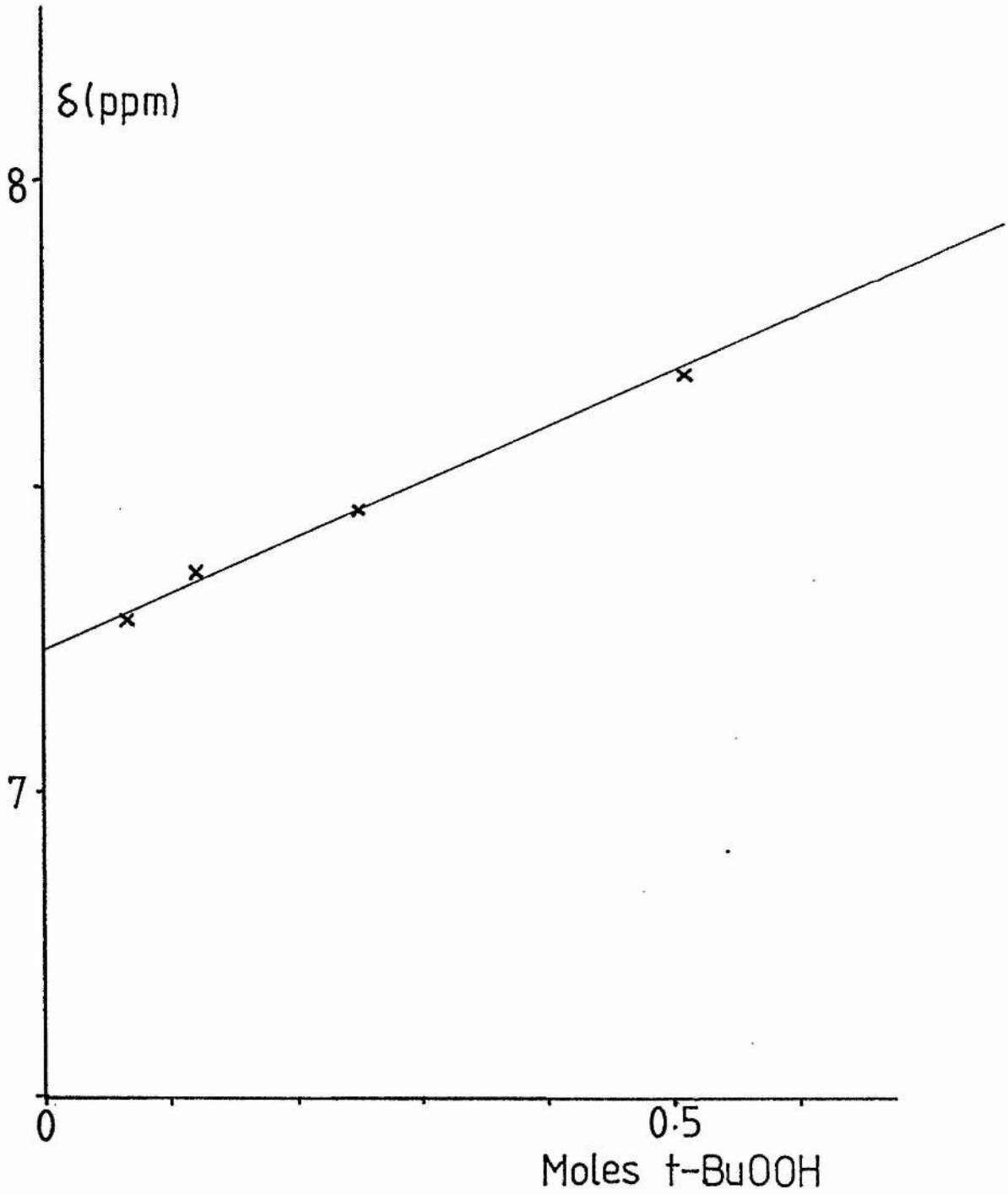
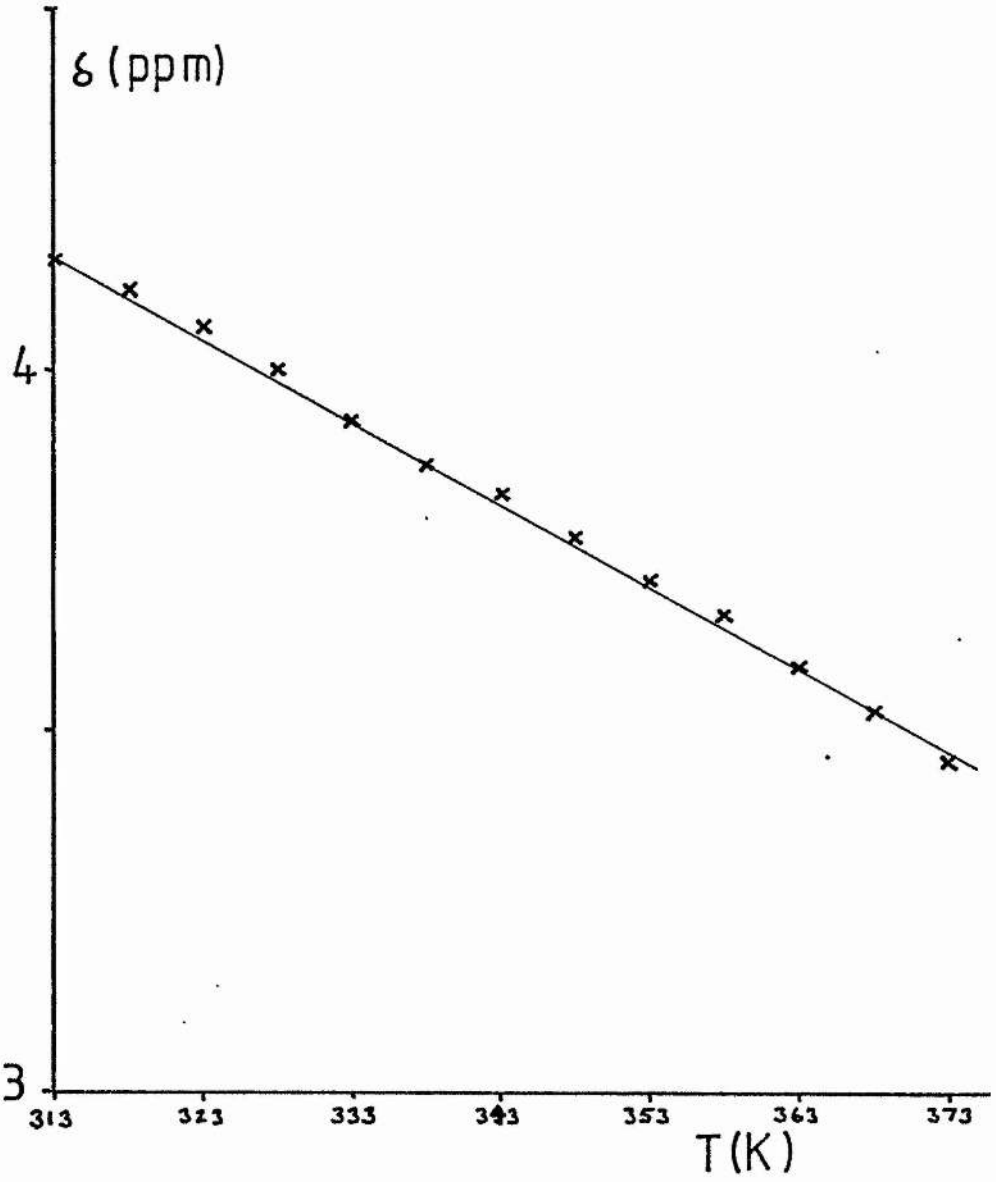


Figure 4.9

Change in NMR chemical shift of hydroperoxy proton with temperature.

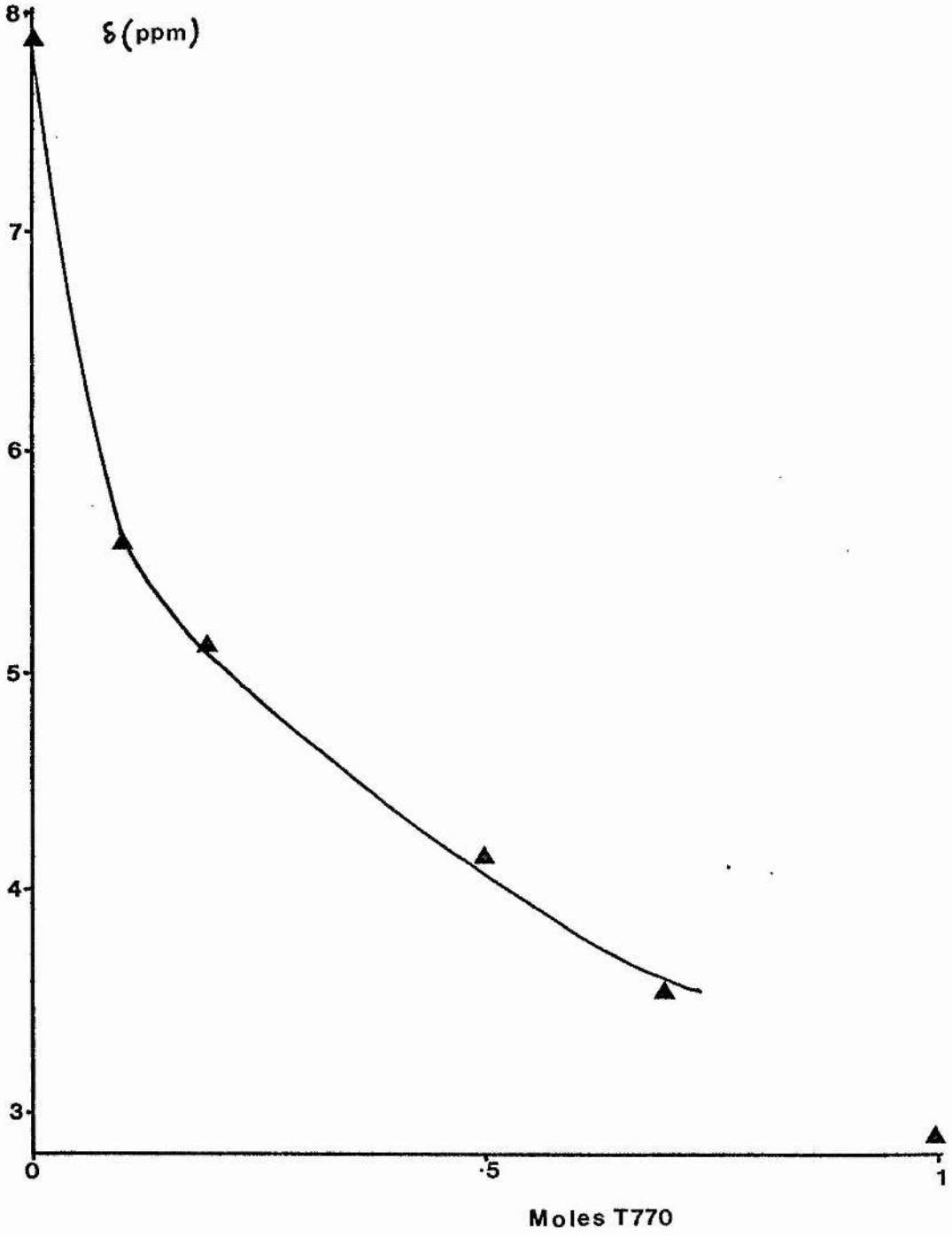


bonding [112]; intramolecular H - bonds are less affected than intermolecular ones by changes in concentration, both types are affected by temperature variations. Since H - bonding involves partial electron transfer from the H to a neighbouring electronegative atom (O, N, or S), the hydrogen experiences a net deshielding effect when H - bonding is strong, and is less deshielded when H - bonding is diminished. These effects may be seen in Figures 4.8 and 4.9, in which the change in chemical shift undergone by dilute solutions of tBuOOH with both concentration and temperature is shown.

Addition of an amine such as HALS to a solution of tBuOOH would be expected to have some effect on the chemical shift of the hydroperoxy proton, if an association had been formed. Using a Bruker 80 MHz NMR Spectrometer, the effect of the addition of various concentrations of Tinuvin 770 on the hydroperoxy chemical shift of a 1.005 mol $dm^{-3}$ solution of tBuOOH in $CCl_4/CDCl_3$ was investigated, with the results shown in Figure 4.10. Such a large change in chemical shift on addition of the hindered amine would seem to suggest a substantial interaction between tBuOOH and HALS, but this is not necessarily so. We have already noted the marked effect of changes of concentration and temperature on hydroperoxide spectra, and it has been quoted [113] that changes of up to 10ppm can occur in making and breaking H - bonds. Unfortunately, limitations of this technique do not allow us to assign quantitative values to the amount of tBuOOH associated with HALS.

Figure 4.10

Change in chemical shift of hydroperoxy proton with concentration of Tinuvin 770.



Carrying out a similar experiment with Chimassorb 944 resulted in the same type of behaviour, but experiments carried out using tertiary amines did not. An experimental run using Tinuvin 622 showed a rapid broadening of the hydroperoxy resonance, but very little change in chemical shift.

Experiments to determine, by NMR, the existence of association between nitroxides and tBuOOH could not be carried out due to the unpaired electron in the radical interfering with the proton resonance signal.

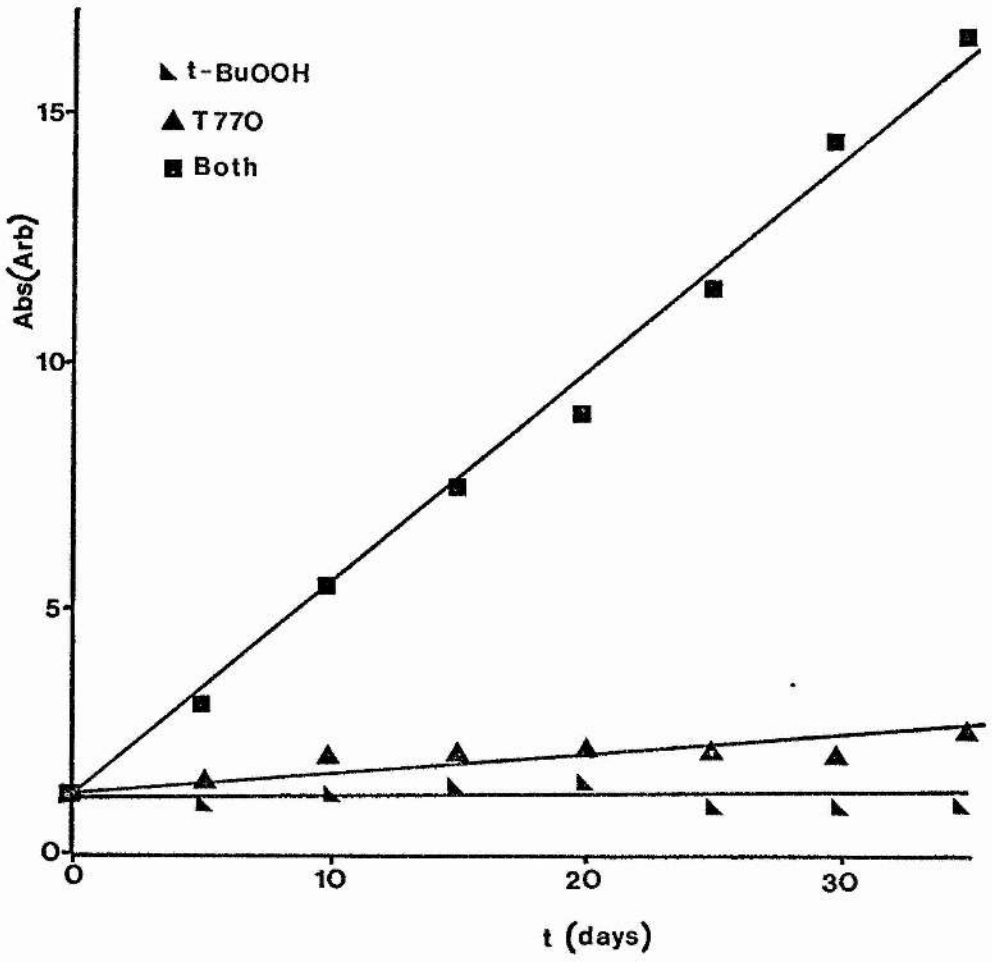
4:2:2 UV/Visible Absorption Spectroscopy

Solutions of HALS in neat tBuOOH were prepared, and exposed to diffuse sunlight. Within three days, the TMP solution had turned dark red, indicating substantial formation of the nitroxide radical; after approximately 20 days the solutions containing Tinuvin 770 and Chimassorb 944 had turned bright orange, indicating that they too were capable of a direct reaction with the hydroperoxide. Of the tertiary HALS, Tinuvin 292 showed a pale orange colour after 40 days, while Tinuvin 622 showed no colour change, even after 100 days.

Having established the occurrence of the reaction between ROOH and HALS, an experiment was carried out on dilute solutions of the substrates. Three solutions were prepared :- a) $1.27 \times 10^{-3}$ mol $dm^{-3}$ tBuOOH in $CHCl_3$; b) $5 \times 10^{-3}$ mol $dm^{-3}$ Tinuvin 770 in $CHCl_3$; c) $1.27 \times 10^{-3}$ mol $dm^{-3}$ tBuOOH plus $5 \times 10^{-3}$ mol $dm^{-3}$ Tinuvin 770 in $CHCl_3$. Using the absorbance at 275nm as an arbitrary marker, changes in the UV/Visible spectroscopic

Figure 4.11

Reaction of tBuOOH and Tinuvin 770 under sunlight - Change in 275nm absorbance.



behaviour of the solutions on exposure to diffuse sunlight were followed using a Unicam SP800 Spectrophotometer. Results are shown in Figure 4.11. As expected, even over a long period of time, Tinuvin 770 shows no change; the tBuOOH exhibits very little change in the 275nm region, but observations of lower wavelengths show that a moderate change takes place. The solution containing both compounds shows a marked change, and shows that there is a definite reaction occouring between the two. It is important to note, however, that this change takes place over a very long period of time.

4:2:3 Infra - Red Spectroscopy

Again using tBuOOH as a model compound, the ability of HALS to form associations with this type of compound was investigated, using the method of Sedlar et al [55]. IR spectra of solutions containing 0.025 mol $dm^{-3}$ of tBuOOH and varying concentrations of the stabiliser (0 - 0.2 mol $dm^{-3}$) in $CCl_4$ were taken, using a Beckman liquid IR cell, on a Perkin - Elmer 1330 IR Spectrophotometer, and the reaction followed by observing the disappearance of the 3540$cm^{-1}$ absorbance attributable to hydroperoxide monomer (See Figure 4.12 for a typical illustration).

For the association, the equilibrium can be described as follows :-

$$ROOH + HALS \rightleftharpoons (ROOH.....HALS)$$

Equilibrium constant K = [ROOH...HALS]/[ROOH][HALS]

From this equilibrium, the K's for association between tBuOOH and the various HALS can be calculated (Table 4.F)

Figure 4.12

Variation of tBuOOH 3540cm$^{-1}$ IR absorption with Tinuvin 770 concentration.

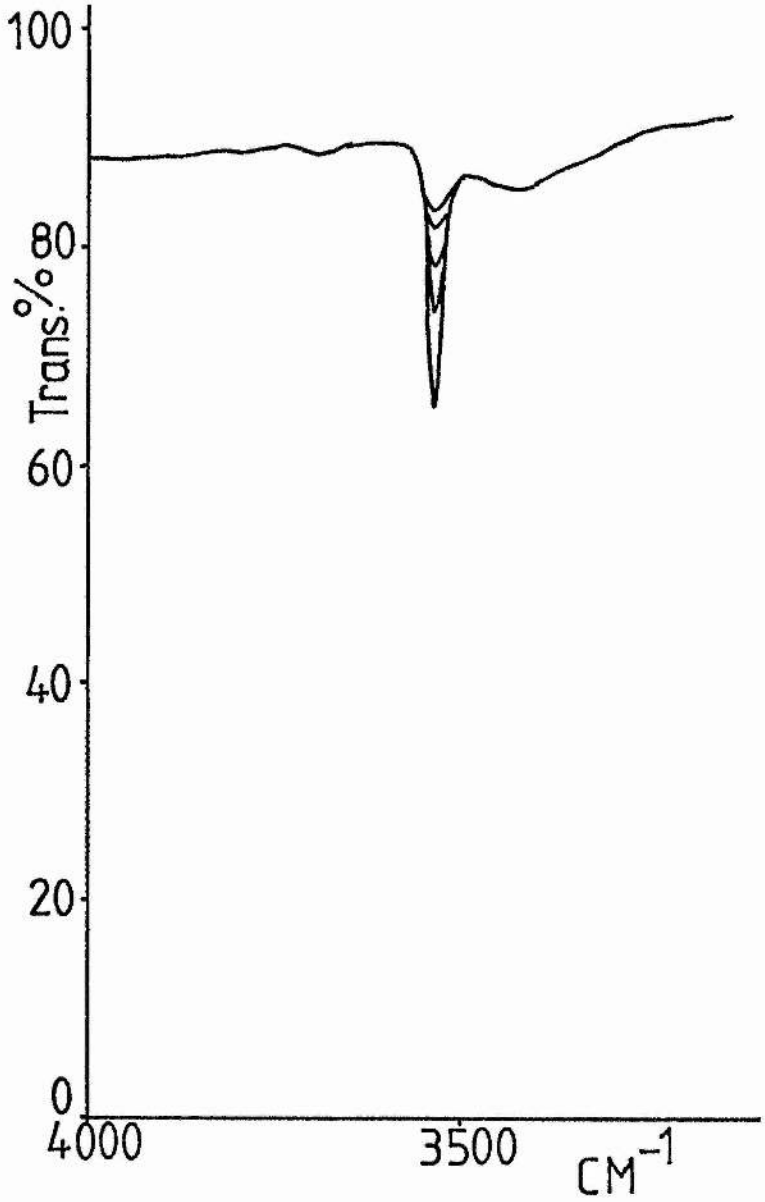


TABLE 4.F

Equilibrium constants, K, for association formation between tBuOOH and HALS.

| Compound | K ($M^{-1}$) |
|---|---|
| TMP | 25 |
| Tinuvin 770 | 27 |
| Chimassorb 944 | 37 |
| Tinuvin 292 | 13 |
| Tinuvin 622 | 3 |
| TMPO | 3 |
| Tinuvin 770 nitroxide | 3 |
| Chimassorb 944 nitroxide | 11 |

The values we have found for K for secondary and tertiary hindered amines are in excellent agreement with values found by previous authors [55,56]. Calculated values for nitroxide association, on the other hand, are substantially lower than those found by Grattan et al [57].

## 4:2:4 Conclusions

Results from NMR spectroscopy indicate that there is some form of association between hydroperoxides and amines, but because of the extreme sensitivity of the chemical shift of hydrogen bonded species, and the limitations of the basic technique, it is difficult to deduce whether a significant association of tBuOOH and HALS exists.

UV/Visible spectroscopy shows that the reaction between HALS and tBuOOH to produce a stable free - radical is viable but slow at reduced concentration. At the level present in a polymer, such a random stoichiometric reaction would be very slow, and might be able to account for the very low proportion of nitroxide present in a degrading sample.

The only method investigated to produce reproducible quantitative data on the association is IR spectroscopy, and this merits closer examination. Equilibrium constants are expressed in the units "per mole" therefore it is crucial to ascertain the concentration of the components which come together to form such a complex. In a poly(propylene) sample, the concentration of hydroperoxide present tends to be in the range $1 - 20 \times 10^{-4}$M [114], while standard amounts of hindered amines added to a

commercial polymer are in the range $10^{-4}$ - $10^{-3}$M. Taking Tinuvin 770 as a typical stabiliser, and applying the above equilibrium, a value of $1.35 \times 10^{-5}$M is obtained for the concentration of the complex. This represents c.1.5% of the original hydroperoxide concentration. Actual values may fluctuate to either side of this, depending on the processing history of the sample, but it is clear that in an actual polymer environment the amount of association formed between Tinuvin 770 and the hydroperoxides in the polymer will be low. In the case of tertiary HALS, which are equally effective stabilisers [48], this figure will be even lower.

These results cast doubt on the importance of the ROOH....HALS association.

## 4:3 Interaction of HALS with Metal Ions.

As has been noted already [26,27,28], trace amounts of transition metals are capable of substantially accelerating photo-oxidation of liquid hydrocarbons. The decomposition of hydroperoxides by millimolar amounts of metal ions such as $Co^{2+}$, $Mn^{2+}$, and $Fe^{2+}$ is quite rapid even at RT [115]; the products in unreactive solvents can be rationalised by :-

$ROOH + M^{n+} \longrightarrow RO. + M^{(n+1)+} (OH^-)$

$ROOH + M^{(n+1)+} \longrightarrow ROO. + M^{n+} (H^+)$

followed by radical chain decomposition in competition

with :- $RO. + M^{n+} \longrightarrow RO^- + M^{(n+1)+}$

If present in excess, however, $M^{n+}$ may compete effectively for RO.. This reaction, together with a similar reduction of peroxy radicals, presumably explains why a low concentration of metal ions is optimal for catalysing autoxidations.

The presence of a variety of trace metals in poly(propylene) has been documented [5], and our own analyses of poly(propylene) films containing various HALS shows the presence of a significant amount of iron (Table 4.G). It is a plausible argu ment to suggest that the trace metal impurities, being mobile species in most cases [5], might act in a similar way in polyolefins to that which they exhibit in liquid hydrocarbons.

The ability of amines to act as electron donors in a variety of organometallic compounds is well known [116]; recently, a possible complexation reaction between a HALS and Fe(III) has been noted [56]. Up till now there has been no study undertaken on the effect of HALS on metal ions, and it was decided to

TABLE 4.G

Analyses of poly(propylene) films for iron, using atomic absorption spectroscopy.

| Additive | Fe (ppm) |
|---|---|
| None | 6 |
| Tinuvin 770 | 13 |
| Tinuvin 622 | 10 |
| Chimassorb 944 | 15 |

instigate such an investigation of this potentially important reaction.

4:3:1 Qualitative Investigation.

As an initial test, aqueous solutions of chloride salts of the first transition series metals were treated with an acetone solution of Tinuvin 770, and any changes in character observed. $FeCl_3$ and $CoCl_2$ proved to be readily soluble in acetone, and were used in this way.

All salts used were of SLR grade, and contained water of crystallisation. Acetone was purified by distillation and drying with calcium chloride; water used was demineralised.

On mixing, the following observations were made :-

1. Ti (III) - Purple solution — white precipitate
2. V (IV) - Pale blue solution — grey/brown precipitate
3. Cr(III) - Bottle green solution — pale green precipitate
4. Mn(II) - Pale pink solution — red/brown precipitate
5. Fe(II) - Pale green solution — dark green precipitate which gradually turned brown /orange.
6. Fe(III) - Yellow solution — orange precipitate
7. Co(II) - Blue solution — pale blue precipitate which slowly turns green
8. Ni(II) - Pale green solution — pale green precipitate
9. Cu(I) - Insoluble in water or acetone
10. Cu(II) - Pale blue solution — blue/green precipitate
11. Zn(II) - Insoluble in water or acetone

In each of the above cases a blank experiment consisting of

addition of acetone only to the aqueous solutions was carried out, with no resultant precipitation.

From these observations it may be seen that Tinuvin 770 is capable of forming a complex, exact nature undetermined, with transition metal ions. The drastic colour changes noted in many cases also indicate the ability of T770 to oxidise the metal ions to higher oxidation states, except in the cases (e.g. Cr, Ni) where such states are unstable; in some cases this change takes place immediately, in others there is some delay.

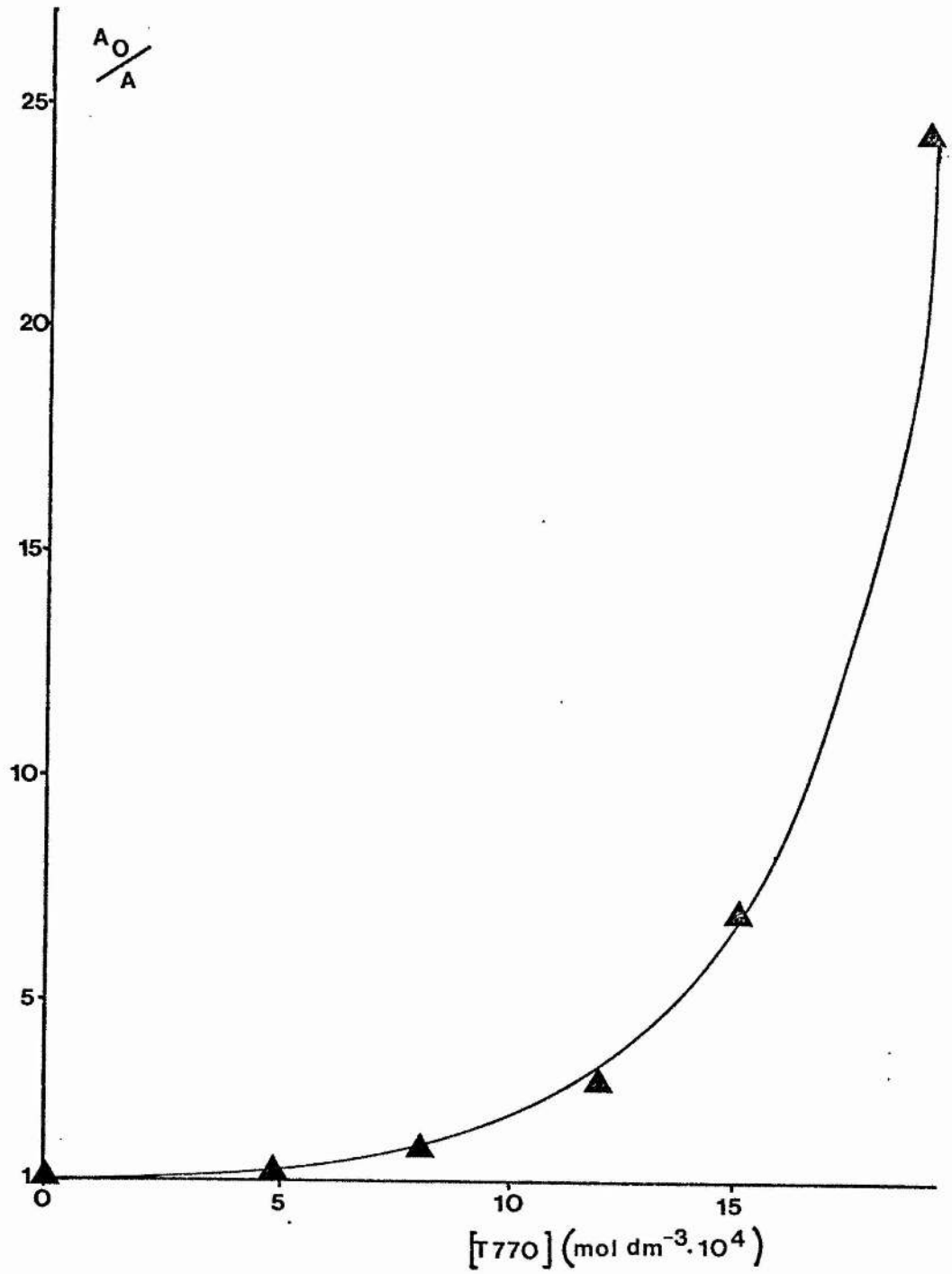
Having established that some form of complexation reaction does occur, it was now necessary to investigate this more fully, using particular metal ions as examples.

4:3:2 Iron (III)

Because of its known presence in polymer systems, iron was chosen as the main element to be investigated. Fe(III) was particularly convenient, in that its chloride dissolves readily in acetone, thereby bypassing any problems which might arise from the spectroscopic study of mixed solvent solutions. Anhydrous $FeCl_3$ was used throughout the experimental series (Fisons, SLR), although comparisons with hydrated material showed no differances in their behaviour. $FeCl_3$ was dissolved in acetone at c. $10^{-3}$ mol $dm^{-3}$, and the additive present varied from $2 \times 10^{-4}$ - $5 \times 10^{-3}$ mol $dm^{-3}$, in most cases. After being allowed to react, in the dark, for 24hrs, samples were centrifuged down and the clear solutions recovered. The reaction was followed on a Unicam SP8 - 150 Spectrophotometer, using the characteristic Fe(III) absorbance at 360nm.

Figure 4.13

Plot of $A_0/A$ for Fe(III) 360nm absorbance vs. concentration of Tinuvin 770.



a)Tinuvin 770 Various concentrations of T770 were dissolved in a 1.13 $10^{-3}$ mol $dm^{-3}$ acetone solution of $FeCl_3$, and the spectra obtained as described above. Plotting the initial 360nm absorbance divided by absorbance at each concentration vs the T770 concentration, the plot shown in Figure 4.13 was obtained. From this it is obvious that, at approx. 2 molar equivalents, T770 has reacted with virtually all the available Fe(III) in solution, and deposited same as an insoluble complex.

b)Chimassorb 944 In a similar experiment to the above, C944 gave essentially the same result, although some difficulty was encountered in obtaining clear spectra, due to the fine, almost colloidal, nature of the precipitate resulting from the reaction. Again, according to the spectroscopic evidence, the metal ion is almost totally consumed by approx. 2 molar equivalents of the HALS.

c)2,2,6,6 - Tetramethylpiperidine On treating samples of the above with $FeCl_3$ / acetone solution, it was noted that no precipitate occured. Spectroscopic evidence shows that the product of this reaction has a low absorbance in the region of the Fe(III) 360nm peak, but exhibits an increasing, though very low, absorbance tail above 400nm (Figure 4.14). The addition of low concentrations of TMP produces a slight attenuation or the 360nm peak, which suggests a change in extinction coefficient.

Figure 4.14

Variation of Fe(III) UV/Visible absorption spectrum with concentration of 2,2,6,6-tetramethylpiperidine.

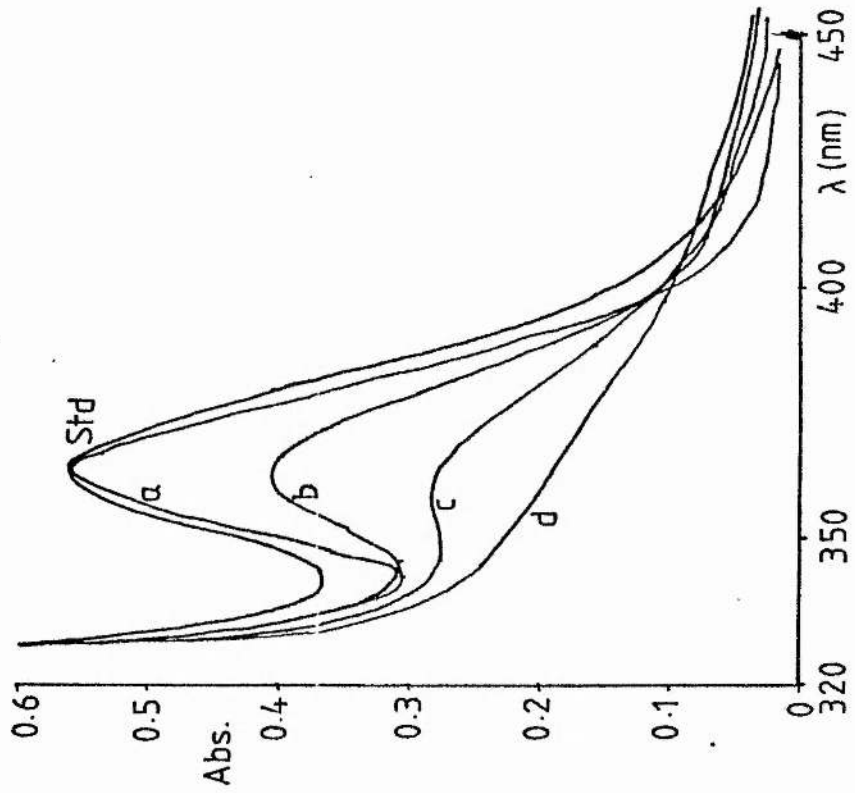


Figure 4.15

Plots of $A_o/A$ for Fe(III) 360nm absorbance vs. concentration of model hindered amines.

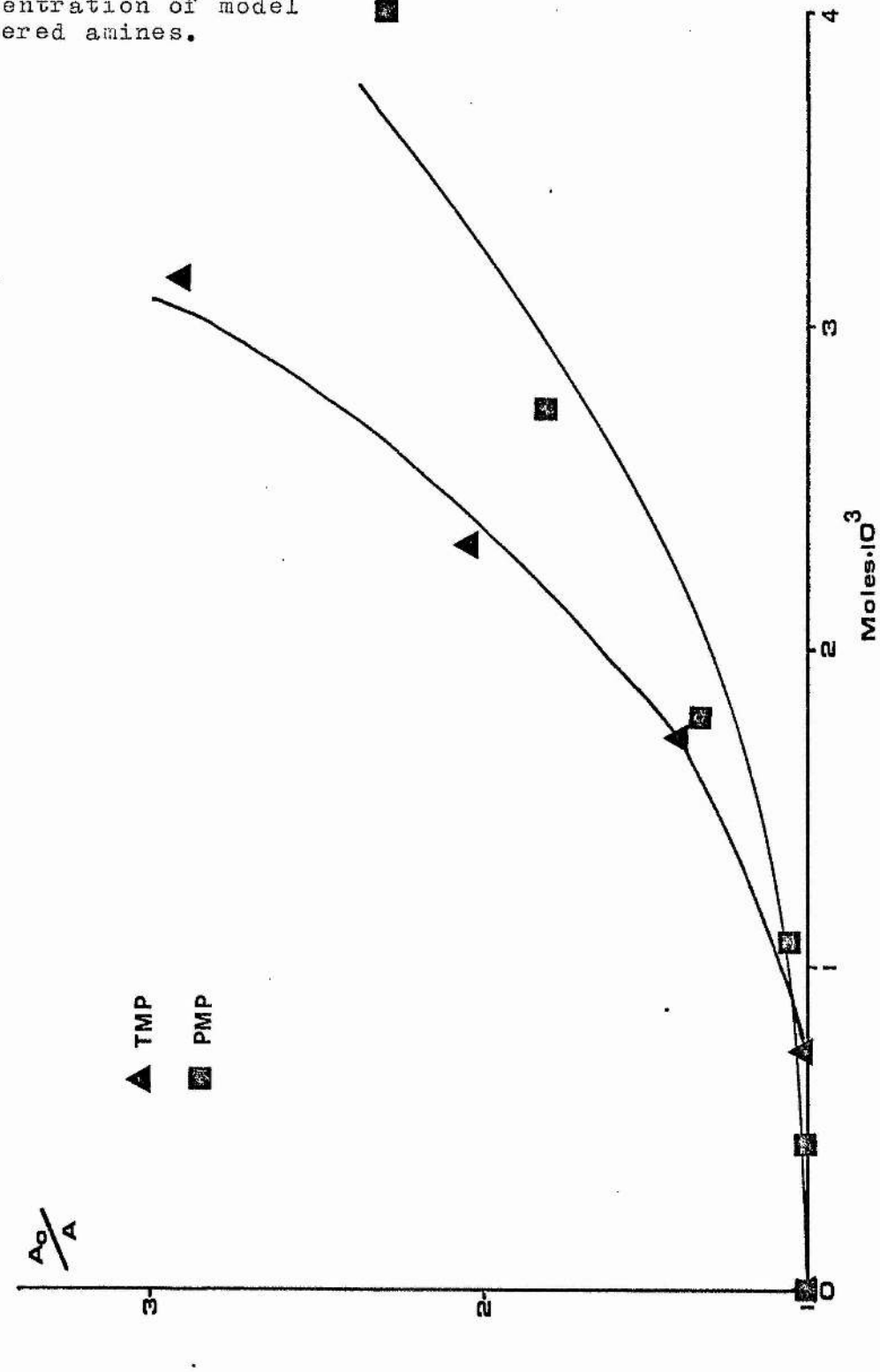
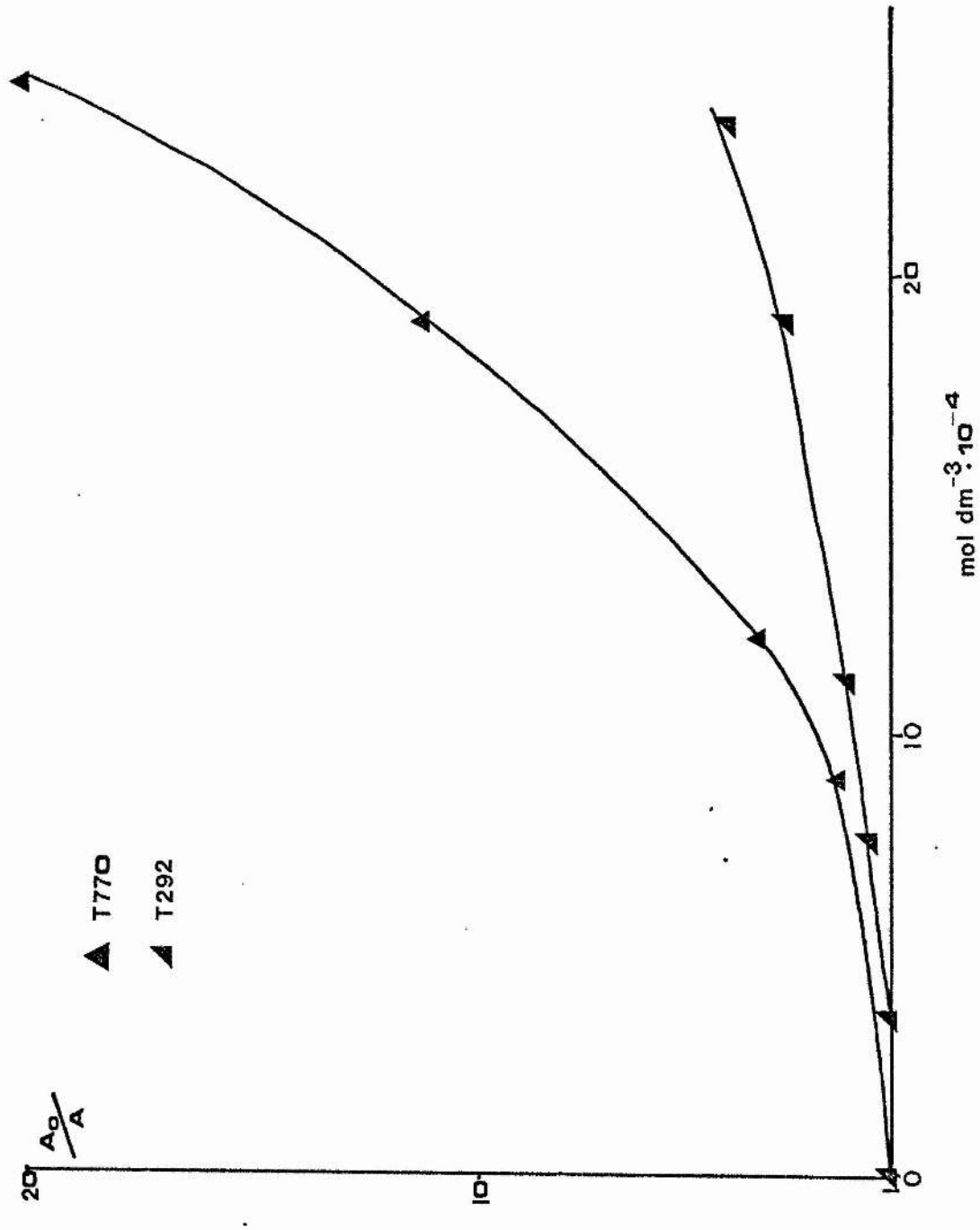


Figure 4.16

Plots of A /A for Fe(III) 360nm absorbance vs. concentration of commercial hindered amine light stabilisers.



c)Comparison of Secondary and Tertiary Amines. It has been noted that tertiary amines can be as effective stabilisers in polymer systems as secondary [48], therefore a series of experiments comparing the ability of secondary and tertiary amines to complex with Fe(III) were undertaken. Figure 4.15 shows the comparitive complexing ability of the two model compounds, TMP and PMP (bearing in mind that $A_0/A$ measurements at high concentration may be affected by the product absorbance). The plot shows the secondary amine to be the better complexing agent, although the difference in the ability is exaggerated by the axes. PMP is still an effective metal ion scavenger.

Figure 4.16 shows a similar comparison plot for T770 and T292.

In order to show a more direct comparison between the complexing abilities of different HALS, a term, $C_{0.5}$, denoting the concentration of HALS required to reduce the 360nm absorbance to half its original intensity, is invoked. Results for the secondary and tertiary amine comparison experiments are shown in Table 4.H. Using this numerical comparison it may be seen that the ability of tertiary and secondary amines to complex with Fe(III) is not as markedly different as the plots suggest. Considering the great difference in relative Fe(III) / HALS concentration between our experiments, and the situation in a polymer system containing trace metal impurities, this difference may not be important. The differences between the $C_{0.5}$ values of the commercial HALS and the model compounds may be due to the bifunctional nature of the HALS.

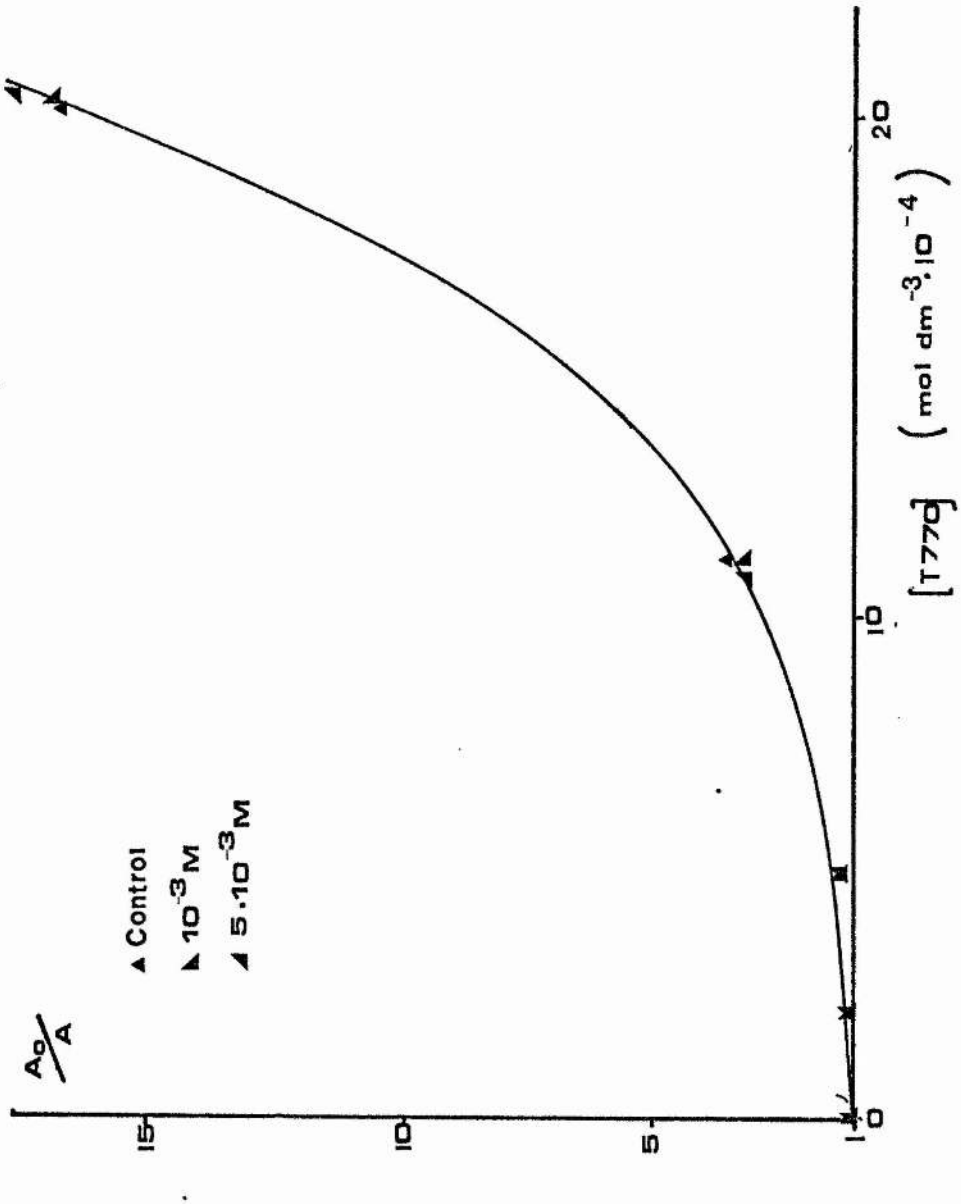
TABLE 4.H

Complexing ability of hindered amines denoted by $C^{0.5}$. Iron concentration throughout equal to $10^{-3}$ mol $dm^{-3}$.

| Amine | $C^{0.5}$ (mol $dm^{-3}$) |
|---|---|
| Tinuvin 770 | $8.50\ 10^{-4}$ |
| Tinuvin 292 | $1.18\ 10^{-3}$ |
| 2,2,6,6-Tetramethylpiperidine | $2.30\ 10^{-3}$ |
| 1,2,2,6,6-Pentamethylpiperidine | $3.30\ 10^{-3}$ |

Figure 4.17

Effect of addition of tBuOOH on the reaction between Fe(III) and Tinuvin 770.



e)Complexing Ability of Nitroxide Radicals Addition of various concentrations of T770NO. to a solution of Fe(III) does not have a marked effect on the UV/Visible spectroscopic characteristics, serving only to slightly attenuate the peak at 360nm. This effect may again be due to a change in the extinction coefficient, with a possible contribution due to the paramagnetic nature of the radical. Similar results were obtained using TMPO and C944NO..

f)Effect of tBuOOH Having already questioned the validity of a stabilisation mechanism involving ROOH...HALS complexation, and taking into account the evidence for ROOH...$M^{n+}$ associations [28], it is now necessary to investigate the effect of the addition of hydroperoxide to the Fe(III) - HALS system.

A $1.00 \times 10^{-3}$ mol $dm^{-3}$ solution of $FeCl_3$ in acetone was prepared and split into three portions; one being used as a control sample, and the others containing $10^{-3}$ mol $dm^{-3}$, and $5 \times 10^{-3}$ mol $dm^{-3}$ tBuOOH respectively. Experiments were carried out adding aliquots of these mixtures to varying concentrations of Tinuvin 770. The results obtained (Figure 4.17) show that the addition of tBuOOH has no effect on the T770 - Fe(III) reaction.

4:3:3 - Iron (II)

It has been suggested by some authors [117] that Fe(II) is a much more important decomposer of ROOH than Fe(III). Looking at the decomposition cycle already cited [115] at the beginning of Section 4:3 this would appear to be logical, taking into account the much lower bond energy of RO - OH compared to ROO - H.

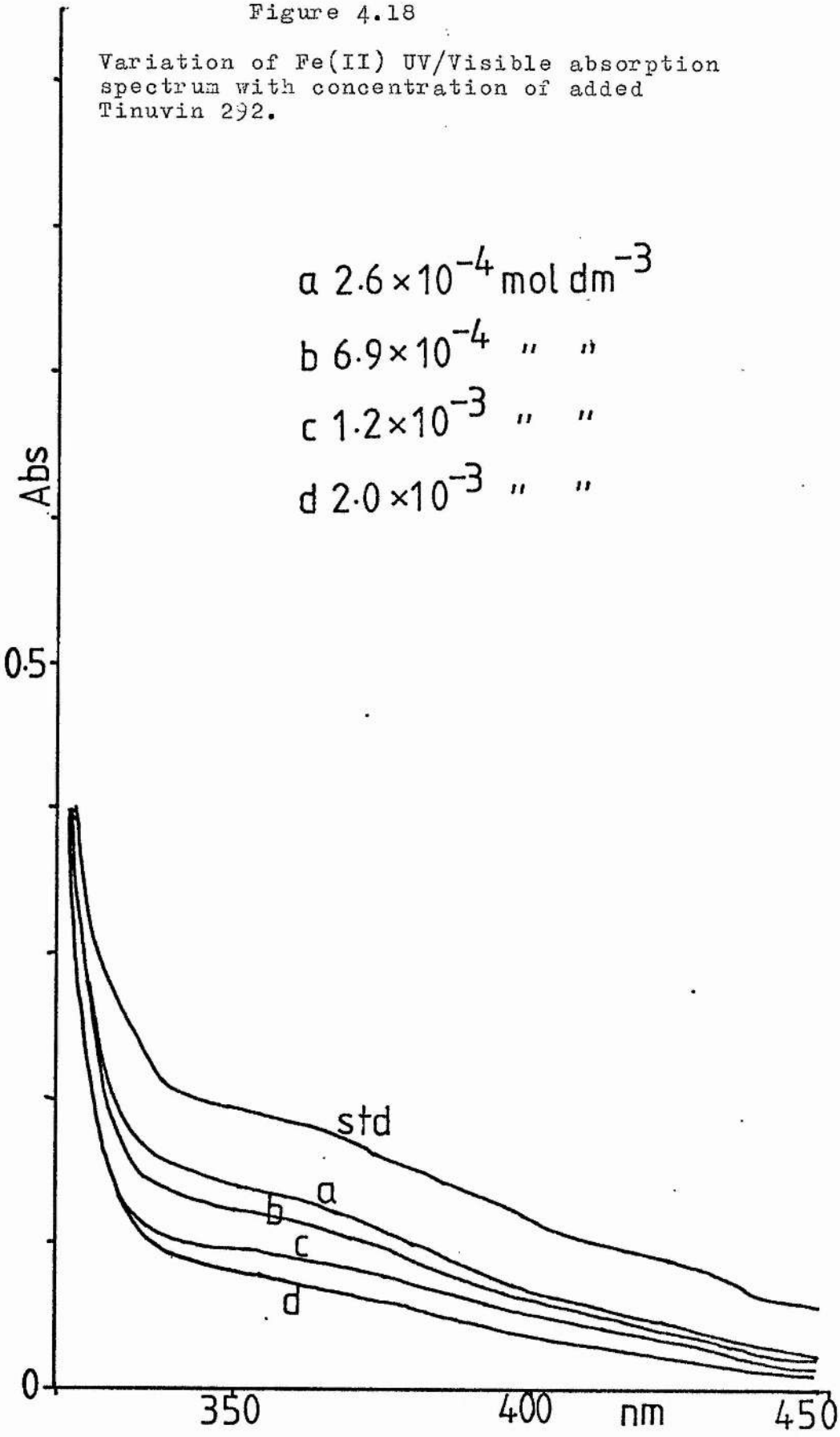
Moreover, Rozantsev et al [118] have intimated that nitroxide radicals can complex with a variety of divalent transition metal species. Taking this evidence into account, it was deemed important to carry out a similar series of experiments to those described above on Fe(II).

In the case of Fe(II) solution phase experiments we encountered the problem of obtaining stable solutions of the ion. $FeCl_2$ does not dissolve in acetone, and its aqueous solutions rapidly oxidise to Fe(III). It was found, after some experimentation, that ammonium ferrous sulphate ($(NH_4)_2Fe(SO_4)_2.6H_2O$; Fisons, SLR) would form relatively stable solutions in water, and it was decided to use this material in experiments.

Approx. $2 \times 10^{-3}$ mol $dm^{-3}$ solutions of the Fe(II) salt were made up in demineralised water, fresh solutions being prepared immediately before each experiment. Acetone solutions of HALS ($4 \times 10^{-4}$ - $10^{-2}$ mol $dm^{-3}$) were prepared. Mixing equal portions of each solution produced the reaction mixture, and halved the concentrations to values comparable to those used in the previous section. In allowing the components time to react, and any precipitate time to settle out to some extent before centrifugation, there was inevitably some deterioration in the Fe(II) aqueous/acetone control solution, therefore spectra tended to be taken after only 5 - 10hrs reaction time, in order to minimise this.

Figure 4.18

Variation of Fe(II) UV/Visible absorption spectrum with concentration of added Tinuvin 292.



Attempts were made to follow the reaction using UV/Visible absorption spectroscopy, but these were generally not particularly useful. Fe(II) does not have a distinct UV absorbance like Fe(III), and very fine precipitates plus instability of Fe(II) solutions also contributed to these difficulties. Close observation of the reactions revealed behaviour of relevance to the stabilising ability of HALS.

a)Hindered Amines On adding the aqueous Fe(II) solution to acetone solutions containing various concentrations of Tinuvin 770, a dark green colour was initially observed, intensity increasing with increasing concentration of T770. After a few seconds, the solutions turned yellow / orange, and within 1min an orange precipitate appeared.

Practically indistinguishable behaviour was noted for Tinuvin 292, and the relevant spectra for this experiment are shown in Figure 4.18 as representitive of the Fe(II) - HALS reaction.

Addition of aqueous Fe(II) solution to acetone solutions of TMP gave the same basic result as above. However, some differences were noted in the longer term behaviour. After approximately 2min, test samples showed definite formation of a precipitate ( *cf.* Fe(III) - TMP reaction)

b)Nitroxide Radicals Varying concentrations of TMPO were treated in a similar manner to the above, and it was noted that, in contrast to the Fe(III) experiments, a small amount of precipitate was observed to form in the test samples. Spectroscopic analyses showed a slight lowering of the overall absorbance for samples containing a low concentration of the radical, but a very broad absorbance centring on 440nm, due to the radical, was noted in samples containing high concentrations of TMPO.

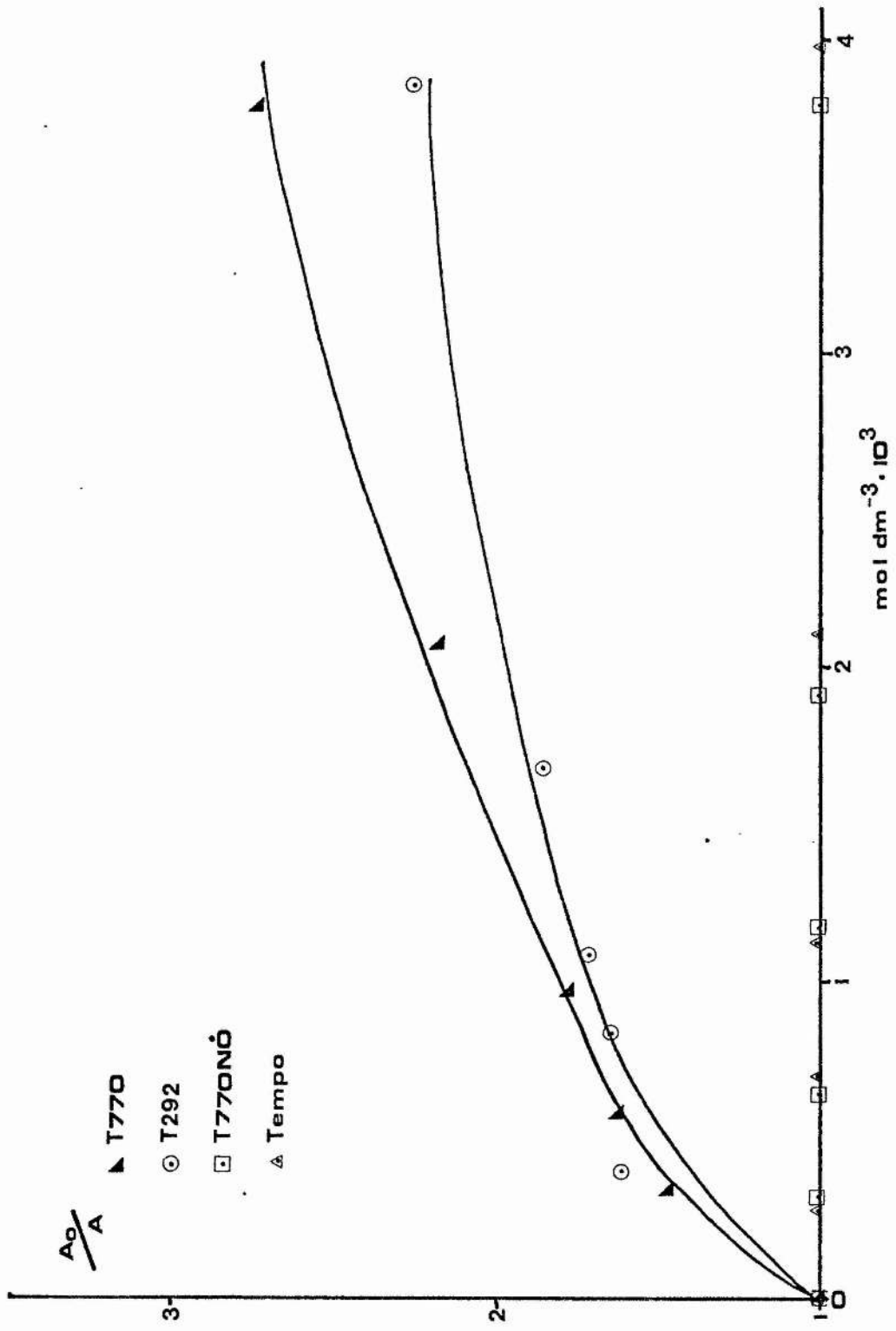
c)Effect of Hydroperoxide Addition of tBuOOH to a solution of Fe(II) rapidly oxidises the ion to Fe(III). Dissolving tBuOOH in an acetone solution of T770 and then adding the aqueous Fe(II) solution did not appear to induce any changes in the nature or rate of the reaction, although the lack of good spectroscopic evidence prevents any definite statement on the subject.

### 4:3:4 Other Transition Metals

a)Cobalt (II) Cobalt chloride ($CoCl_2.6H_2O$; Fisons, SLR) is readily soluble in acetone, producing a deep blue solution. UV/Visible absorption spectroscopy reveals peaks at 676 and 576nm, and a pronounced shoulder at c.634nm. Lying as it does, adjacent to iron in the first transition series, and reversing the stability of its oxidation states (Co(II) stable, Fe(III) stable), it was thought to be of interest to undertake a short investigation into the effect of HALS on the cobalt ion.

Figure 4.19

Plot of A /A for Co(II) 676nm absorbance vs. concentration of various additives.



Using a similar experimental proceedure to that described for Fe(III), aliquots of a $1.02 \times 10^{-3}$ mol $dm^{-3}$ solution of Co(II) were added to varying amounts of T770, T292, T770NO., and TMPO. A pale blue precipitate resulted, and the spectra of the clear solutions remaining after centrifugation gave the data plotted as Figure 4.19. It was noted that, in the case of Co(II), addition of a HALS causes a red shift of the entire spectrum by some 18nm. This appears to be a genuine erfect on the Co(II) absorption spectrum itself, and not due to product; in consequence, the $A_0$ / A vs [HALS] plot is produced with $A_0$ at 676nm, and A measured at 694nm. $C^{0.5}$ values, calculated from Figure 4.19, are $1.44 \times 10^{-3}$ mol $dm^{-3}$, and $2.24 \times 10^{-3}$ mol $dm^{-3}$ for T770 and T292 respectively. It will also be noted that the addition of higher concentrations of HALS does not lead to a complete disappearance of the Co(II) absorbance, but appears from the plot to reach a plateau level of residual free Co(II).

Addition of TMPO and T770NO., up to a ratio of 5 molar equivalents, does not significantly alter the spectral characteristics of the Co(II) solution.

On allowing the samples to stand, in the dark, for 48hrs, it was observed that some of the blue precipitate had changed colour to a greenish - blue shade, indicative of a slow change in oxidation state of Co(II) to Co(III). Perhaps this much slower conversion to the higher oxidation state, due to the greater stability of Co(II), can explain the differences in complexation behaviour exhibited by iron and cobalt.

b)Ruthenium (III) Having established the generality of the HALS - $M^{n+}$ reaction for the first transition series, a final experiment was carried out to test the ability of HALS to complex with the larger transition metals of the second row. Ruthenium, being the second row analogue of iron, was chosen as a representative element.

$RuCl_3$ (Aldrich) dissolves readily in acetone. $9.98 \times 10^{-4}$ mol $dm^{-3}$ Ru(III) in acetone produced a deep wine solution which, under UV/Visible absorption spectroscopic analysis, showed a discrete peak at 406nm, which was used to follow the subsequent reaction.

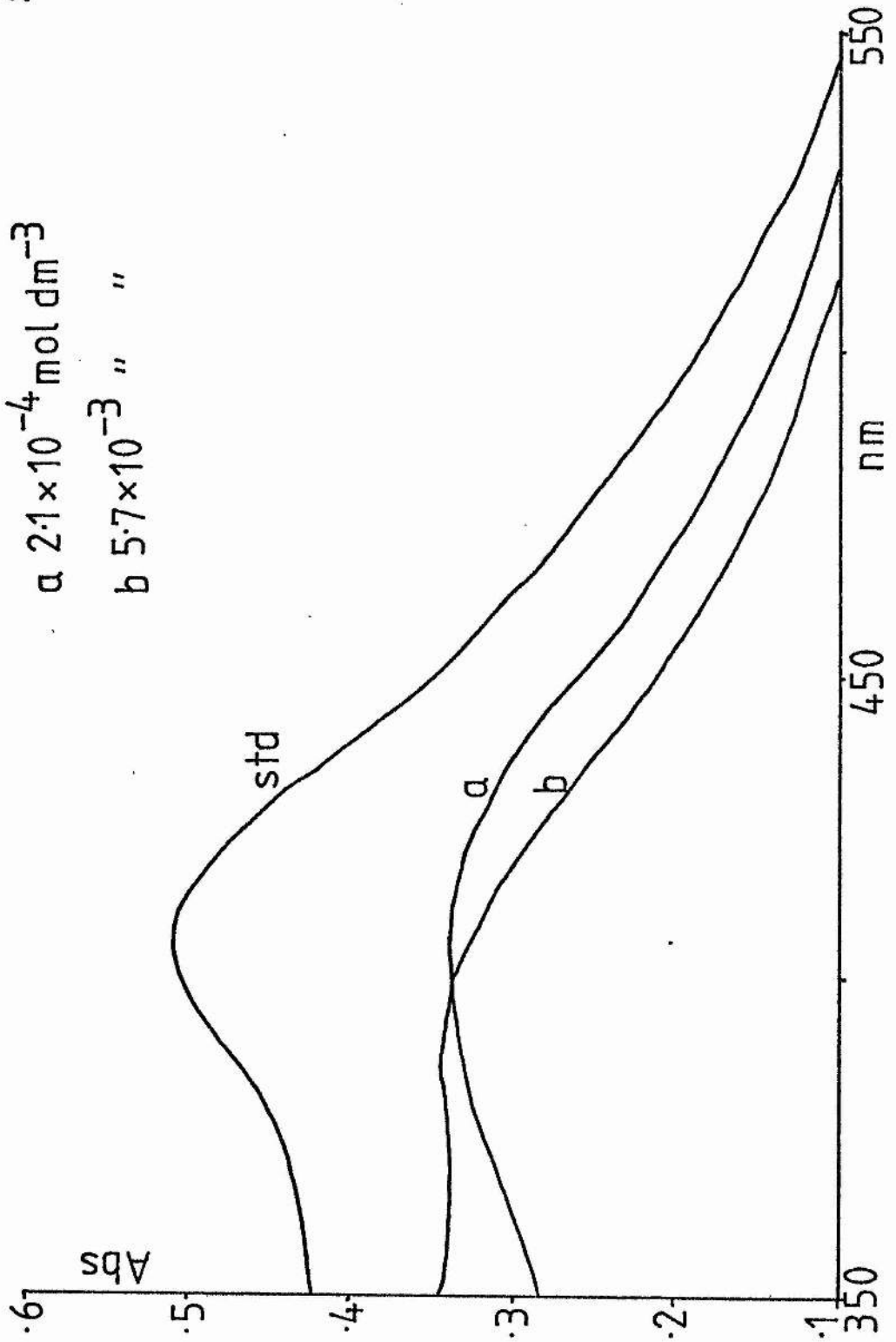
Addition of aliquots of the solution to various amounts of T770 showed that a reaction does indeed take place; a fading of the colour to a more yellowish shade occoured, accompanied by a very fine dark green / black precipitate. Centrifugation failed to eliminate this precipitate in most cases, and hence only samples containing the lowest and highest concentrations of T770 were capable of being spectroscopically analysed (Figure 4.20). These observations confirm that a complexation reaction does occur.

Ru(III) is known to form complexes with amines, and these tend to be brown or green in colour [119], while Ru(IV) is unstable with respect to Ru(III).

## 4:3:5 Conclusions

Figure 4.20

Variation of Ru(III) UV/Visible absorption spectrum with concentration of added Tinuvin 770.



Transition metal impurities in trace amounts, such as have been shown to exist in manufactured polyolefins [5], are known to cause enhancement of autoxidation in hydrocarbon systems [26,117]. This can be caused by the ability of metal ions of variable valence to enter into a redox cycle with hydroperoxide [115] to produce radicals which can then abstract hydrogen from the substrate to continue the autoxidation process, or by absorption and transfer of energy from electronically excited states of the transition metal species.

We have shown in this section that HALS have the ability to complex strongly with such species. While, due to either precipitation of product or juxtaposition of product and reactant absorbances, it is not possible to calculate meaningful association constants, the evidence presented suggests that these will be high.

The interconversion of oxidation states also brought about by HALS has an important bearing on the efficiency of any metal catalysed breakdown of ROOH, as it will greatly affect the redox cycle.

## 5. DIFFUSION EFFECTS

### 5.1 Additives and Impurities

We have already noted, when considering the possibility of HALS taking part in association reactions with various impurities in a polymer matrix, the problem of mobility of such compounds, i.e. their ability to diffuse through a polymer. While it may be conjectured that such diffusion might become a significant factor in the melt phase, it might also be considered that associations of the type envisaged, not involving full chemical bond formation, would be hampered by the high temperature; therefore the process of diffusion, particularly in the context of photo-oxidation, has to be examined at lower temperatures.

Diffusion coefficients are found to be dependent on temperature, polymer morphology, and concentration of diffusant [39]. As the latter factor only tends to apply at high additive concentration, it can be neglected in the case of polymer stabilisers. The diffusion coefficient itself is expressed in terms of an activation energy $E_D$ in the form of the Arrhenius equation [120] :- $D = D_0 \exp(-E_D / RT)$, where $D_0$ is proportional to the square of the molecular diameter of the diffusing molecule; and $E_D$ is proportional to the molar volume of the diffusing species, and is related to the polymer morphology.

Billingham and Walker [39] have shown that the molecular weight of the stabiliser will have a profound effect on the diffusion coefficient. Using results quoted for diffusion of 2-hydroxy-4- octadecoxybenzophenone in isotactic poly(propylene), it is possible to obtain an approximation of the diffusion

behaviour of Tinuvin 770, the two compounds having virtually the same molecular weight. Using this data in the above Arrhenius equation, and taking the temperature to be 298K, a value of $1.5 \times 10^{-10}$ $cm^2$ $s^{-1}$ was obtained for the diffusion coefficient.

The importance of diffusion by a stabiliser in its photoprotective role has yet to be convincingly demonstrated. Oxygen has a diffusion coefficient of c.$10^{-7}$ $cm^2$ $s^{-1}$ at 298K in high density poly(ethylene) [121]; the large difference between this and that of the stabiliser might be offset by a high concentration of stabiliser in the system [122], but we have already stated that HALS, and particularly the nitroxide radicals which are liable to be active in the radical scavenging role, are present in very low concentration. Even types of stabiliser which are used in higher concentration (1 - 5 wt%) show little or no change in stabilising ability in going from the free additive to copolymerised species [123,124,125]. Stabilisers tend to accumulate in the amorphous zones of a polymer matrix, and this may increase the operational concentration of stabiliser in these photo-oxidation sensitive regions.

Another factor which must be considered along with this argument, is the compatability of a stabiliser with the polymer matrix it has been "assigned" to protect. Bain [126] has noted that antioxidant and UV stabiliser effectiveness may depend not only on chemical behaviour, but also on the solubility and diffusivity of a stabiliser. The same author [127] noted that the equilibrium solubility of bisphenol type stabilisers in poly(ethylene) is only c.2% of the original formulation dosage. Solubility also decreases with increasing molecular weight.

Actual physical loss of additive from a polymer sample can be a serious problem, and Calvert and Billingham have made careful attempts to explain the significance of such phenomena [39], and to produce a theoretical model [40]. As yet there has been no study of the diffusion behaviour of hindered amines reported in the literature. Tozzi et al [128] have shown that T770 has low compatability with poly(propylene), and is easily leeched from fibre and film samples; poly(2,2,6,6-tetramethyl-4-piperidylaminotriazine), however, is very compatable and persistent in poly(propylene).

In the case of high MW stabilisers, the above observations would seem to suggest that stabiliser diffusion to an active site will be a very slow process. On the other hand, it might be that the active site or impurity may diffuse towards the stabiliser, or some compromise situation. The hydroperoxides present in a polyolefin are there as a result of oxidation of the hydrocarbon substrate and are therefore attached to the polymer backbone. The movement of these species within the matrix will be very limited, their "volume of freedom" being restricted by the random coil motion of the polymer chain. Even at relatively elevated temperatures, the mobility of a polymeric hydroperoxide will be strictly limited. This, coupled with the low initial concentrations of such species [114], would make it extremely unlikely for them to diffuse towards a stabiliser molecule. On the other hand, free transition metal impurities are very small, mobile, species, and we have already shown thet the diffusion coefficient of a species is dependent on its molecular weight and molecular volume. It is conceivable then that metal species can diffuse rapidly through the polymer matrix to encounter and react

with HALS.

This brief survey of the diffusing ability of additives and impurities, coupled with the evidence provided in the previous chapter, makes a strong case for the metal ion - HALS complexation being an important photostabilising mechanism.

## 5:2 Oxygen - Theoretical Model.

### 5:2:1 Introduction

In the previous section we briefly looked at the ability of impurities and additives to diffuse through a polymer matrix, and it was seen that impurities such as hydroperoxides and carbonyls, which are attached to the polymer backbone, were unlikely to be mobile to any appreciable extent. It was also noted, by comparison with other stabiliser species of similar molecular weight, that HALS would be unlikely to diffuse to impurity sites rapidly enough for this to be an effective contributor to the stabilising mechanism. In the case of $O_2$ however, we are dealing with a very different situation. The small molecular diameter and reactive nature of oxygen make it a highly mobile and effective scavenger of alkyl radical sites, hence establishing the autoxidation cycle.

Although $O_2$ will rapidly diffuse through a polyolefin, there will be certain situations in which the rate of diffusion will become important to the overall oxidation kinetics. For instance, in a thick polymer film, near the centre of the sample, there may occur a situation in which the oxygen present is being consumed in a chemical reaction faster than it is diffusing from the outside atmosphere to the reactive sites; in this case the

diffusion of $O_2$ becomes the rate determining step of the oxidation reaction.

A number of theoretical models have been developed to relate the effects of oxygen diffusion and film thickness to the rate of oxidation of a polyolefin [129,130,131,132], but on closer inspection, each of the literature models appears to suffer from one or both of two major discrepencies:-

a) Even though it is generally assumed that the rate of $O_2$ absorption is diffusion controlled from the film surface [130,132], it is also agreed that, in the case of thin films, the rate is linearly proportional to the film thickness. The rate in this latter case is thus considered to be independent of diffusion effects. An explanation of this apparent paradox is required.

b) The diffusion effects inherent in a polymer film are generally expressed by a differential equation according to Fick's laws of diffusion [133]. The solution to this equation is determined by applying suitable initial and final boundary conditions relevent to the problem under consideration. (The use of Laplace transformation often makes a solution possible in a straightforward way.). In applying these boundary conditions, most authors [129,130,131,132] set the initial condition that at time zero the concentration of $O_2$ in the sample film is zero, i.e. until the experiment begins there is no oxygen in the sample. This is clearly not the case in the practical situation of an oxidising polymer film; in this case one would expect there to be an equilibrium concentration of $O_2$ throughout the film

before the oxidation reaction commences.

The model considered in the following theoretical analysis of the problem is that of oxygen diffusing into a solid polymer film, and being consumed by a first order or pseudo - first order chemical reaction. If a thick film is considered as being symmetrical about the midpoint, then it is proposed that there are two zones; a diffusion free zone at the surface (both faces of the film), beneath which a diffusion controlled zone extends to the midpoint of the sample thickness. This can be seen more clearly as described below, and in Figure 5.1.

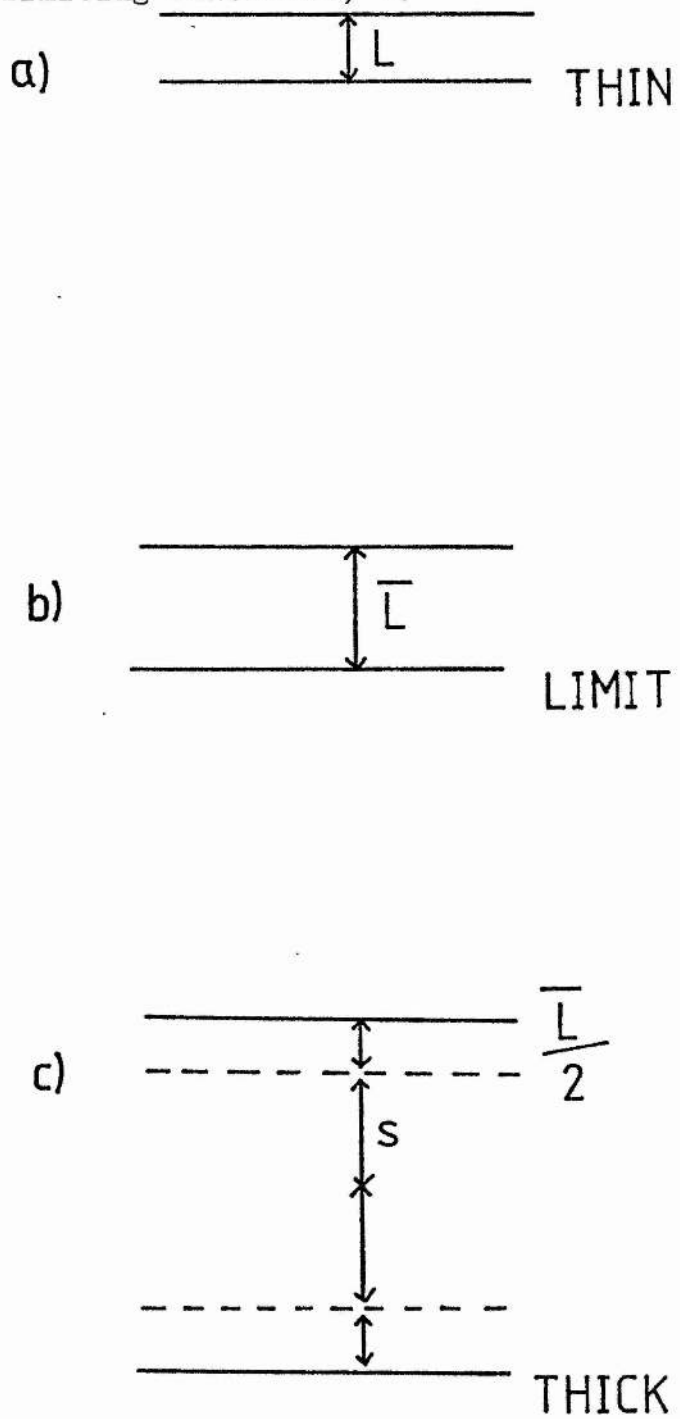
1) Thin film - In this case we have a film of thickness L in which diffusion of $O_2$ is not a limiting factor on the oxidation reaction.

2) Limit film - Here we introduce a new term "$\bar{L}$". This is defined as the Limiting Thickness of a polymer film, and refers to the maximum thickness a sample can attain before $O_2$ diffusion effects begin to manifest themselves in the mathematical model of the oxidation reaction. A full derivation of the mathematical concept of $\bar{L}$ is given later in the chapter.

3) Thick film - The thickness of the film having reached a value greater than $\bar{L}$, we now have a volume in the centre of the film where diffusion of oxygen to reactive sites is the rate determining step of the oxidation reaction. The boundary conditions used (see Section 5:2:3) mean that we measure the various reaction parameters (conc. $O_2$, rate, etc.) from the film surface to its midpoint therefore we define the diffusion

Figure 5.1

Schematic representation of definition of Limiting Thickness, $\bar{L}$.



controlled zone as extending from the bottom of the diffusion free zone (L/2) to the centre of the film, and this is assigned the value "s". This emphasis on the symbols used to define the different zones of the film is necessary since the mathematical model which follows will deal with these zones seperately at first, and only later will a complete equation be proposed.

In the following sections we will derive theoretical solutions for the concentration distribution of $O_2$ in the diffusion controlled zone, the limiting thickness of the diffusion free zone, the total rate of absorption of $O_2$, and the related induction time.

5:2:2 Theory of Diffusion with Chemical Reaction.

The problem which we now consider, is the determination of the rate of absorption of oxygen within a polymer film of planer surface and uniform thickness. The film is exposed to $O_2$ on both faces, external pressure being maintained at a constant value throughout the reaction. Right away let us define the more practical initial condition discussed in the previous section, i.e. in our model we start off with $O_2$ initially present in the film at concentration $C_0$, which is in equilibrium with the external pressure and surface concentration.

The following assumptions are made before we define the basic Fickian equation for diffusion with reaction:-

a) Rate of $O_2$ consumption proceeds at a rate dependent on and proportional to its concentration in the film, obeying first order kinetics.

b) The diffusion coefficient, D, of $O_2$ in the film is independent of $O_2$ concentration.

For any point in the film we may write :-

$$\frac{\partial C(x,t)}{\partial t} = D\left(\frac{\partial^2 C(x,t)}{\partial x^2}\right) - kC(x,t) \qquad 1$$

Where $C(x,t)$ is the concentration of $O_2$ at a given time t and given depth x into the film, where the x direction is defined as perpendicular to the faces of the film, and k is the first order rate constant.

A simplified solution to the differential equation 1 can be obtained by assuming a steady - state condition is reached and maintained in a short reaction time, i.e. $\partial C/\partial t = 0$.

5:2:3 Exact Solution.

As stated previously, the solution to equation 1 can be obtained by application of the Laplace transform, coupled with the relevent initial and final boundary conditions. The boundary conditions which we used to solve 1 are, as noted already, different from those applied by previous authors. These are as follows :-

$C = C_0$ at x=0 and t 0

$C = C_0$ at all x and t=0

$C = 0$ at $x = \infty$ and t=0

Where the terms are as defined above, the solution to equation 1 is given by :-

$$C(x,t) = C_0 \{\exp(-kt)\,[1 - \mathrm{erfC}(x/2\sqrt{Dt})]\}$$
$$+C_0/2\,\{\exp(x\sqrt{k/D})\,\mathrm{erfC}[x/2\sqrt{Dt} + \sqrt{kt}]\}$$
$$+C_0/2\,\{\exp(-x\sqrt{k/D})\,\mathrm{erfC}[x/2\sqrt{Dt} - \sqrt{kt}]\} \qquad 2$$

It must be stressed at this point that this equation applies only to the diffusion controlled zone. From equation 2 a theoretical picture can be built up of the $O_2$ concentration in the film. The concentration gradient is dependent on two variables - film thickness, and time. From this expression it is possible to derive equations to define the total amount of gas reacted with the film, Q(R), and the rate of reaction of $O_2$ with the film, dQ(R)/dt.

a) Q(R) - The total amount of $O_2$ which would react with a polymer film in a time t, is given by the integral of kC(x,t) over the limits x=0 to x=s, and t=0 to t=t. Carrying out this double integration we obtain the solution :-

$$Q(R) = sC_0\,[1 - \exp(-kt)\,\{1 - \mathrm{erfC}(s/2\sqrt{Dt})\}]$$
$$+ C_0\sqrt{Dt/\pi}\,[\exp(-kt)\,\{3 - 2\exp(-s^2/4Dt)\}]$$
$$+ C_0 t/2\,\sqrt{Dk}\,[\exp(s\sqrt{k/D})\,\mathrm{erfC}\{s/2\sqrt{Dt} + \sqrt{kt}\}$$
$$-\exp(-s\sqrt{k/D})\,\mathrm{erfC}\{s/2\sqrt{Dt} - \sqrt{kt}\}]$$
$$+C_0 t/2\,\sqrt{Dt}\,[\mathrm{erfC}(-\sqrt{kt}) - \mathrm{erfC}(\sqrt{kt})]$$
$$- C_0\sqrt{Dk}/2\,\{1 - \mathrm{erfC}(\sqrt{kt})\}$$
$$+ C_0\sqrt{Dt/\pi}\int_0^t \exp(-kt - s^2/4Dt)\,\{\sqrt{kt} + 1/\sqrt{kt}\}\,dt \qquad 3$$

b) dQ(R)/dt - The rate of consumption of $O_2$ is given by the integral of kC(x,t) over the limits x=0 to x=s. Carrying out this integration, we obtain :-

$$dQ(R)/dt = kC_0\,\{\exp(-kt)[s\{1 - \mathrm{erfC}(s/2\sqrt{Dt})\}$$

$$+2\sqrt{Dt/\pi}\ \{\exp(-s^2/4Dt - 1\}]\}$$

$$+ C_{0/2}\sqrt{Dk}[\exp(s\sqrt{k/D})\ \mathrm{erfC}\{s/2\sqrt{Dt} + \sqrt{kt}\}$$

$$- \exp(-s\sqrt{k/D})\ \mathrm{erfC}\{s/2\sqrt{Dt} - \sqrt{kt}\}]$$

$$+ C_{0/2}\sqrt{Dk}\ \{\mathrm{erfC}(-\sqrt{kt}) - \mathrm{erfC}(\sqrt{kt})\} \qquad 4$$

It is necessary to note that the above equations (3 and 4) apply to the quantity Q(R), which is the amount of gas which has chemically reacted with the polymer sample. To obtain the amount of gas physically absorbed by the film under the same circumstances, we must construct a Mass Balance Equation. Let Q(A) equal the total amount of gas absorbed by the film; at any time this quantity will be given by the sum of the gas reacted, Q(R), plus the amount of gas present in the film, Q(T), less the amount present in the film at time zero, Q(0), i.e. :-

$$Q(A) = Q(R) + Q(T) - Q(0) \qquad 5$$

5:2:4 Approximate Solution

As stated previously, the $O_2$ concentration in a polymer film is dependent on two factors; time, and thickness. Calculation of the oxygen concentration, C(x,t), from equation 2 for a fixed depth into a polymer film with varying time was carried out, inserting the values noted below into the equation.

$x = 0.001\text{cm}$

$k = 1\text{s}^{-1}$

$D = 10^{-5}\text{cm}^2\text{s}^{-1}$

$C_0 = 10^{-3}\text{cm}^3(\text{STP})\text{cm}^{-3}$

From the mathematical analysis, and as shown graphically in Figure 5.2a, at sufficiently high values of t the value of C(x,t) became constant, i.e. a steady - state situation applies. Taking equation 2 as a three part solution, increasing t rapidly

Figure 5.2

Comparison of exact and approximate solutions for the value of C(x,t) - Variation of oxygen concentration with time.

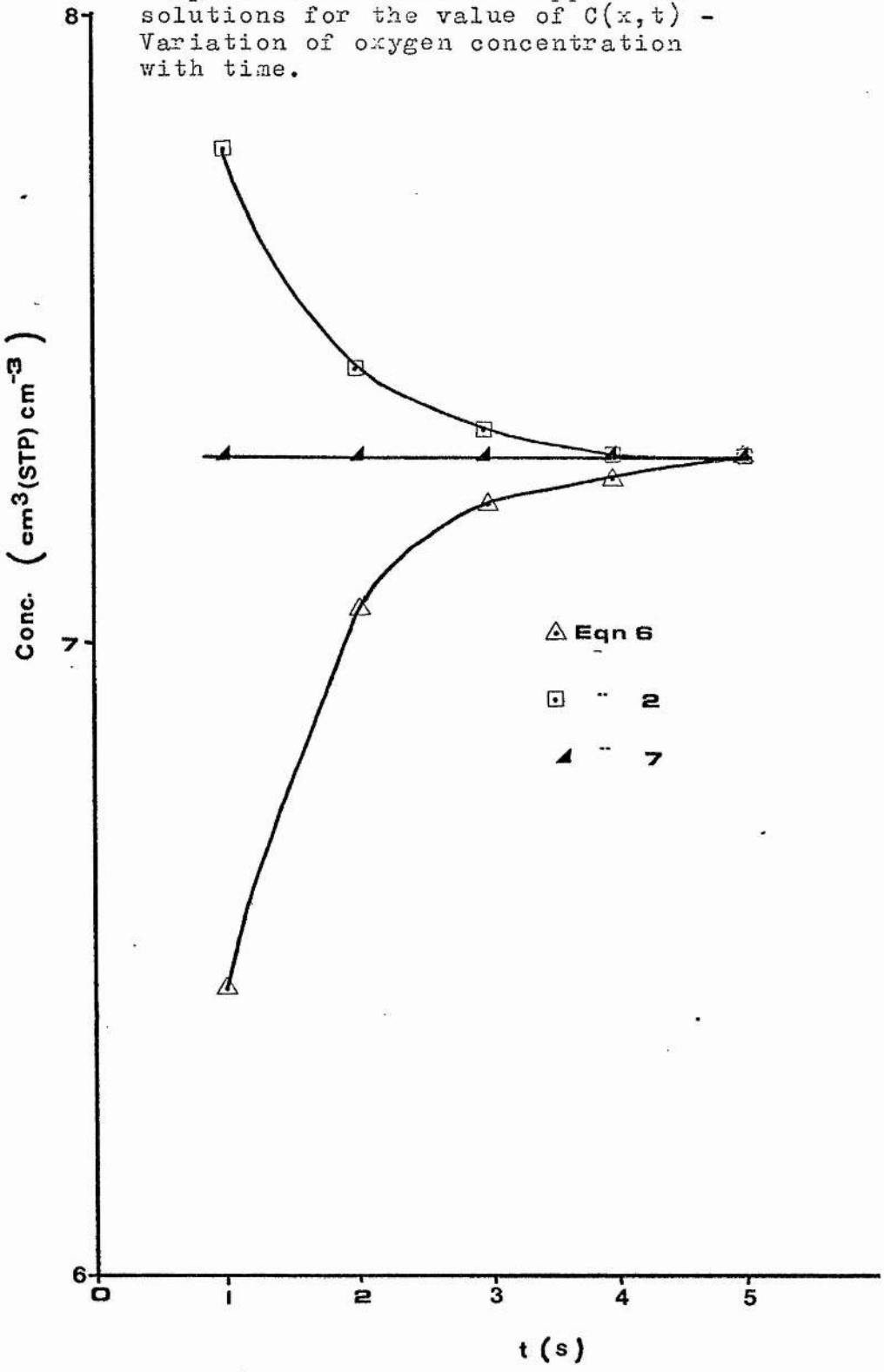
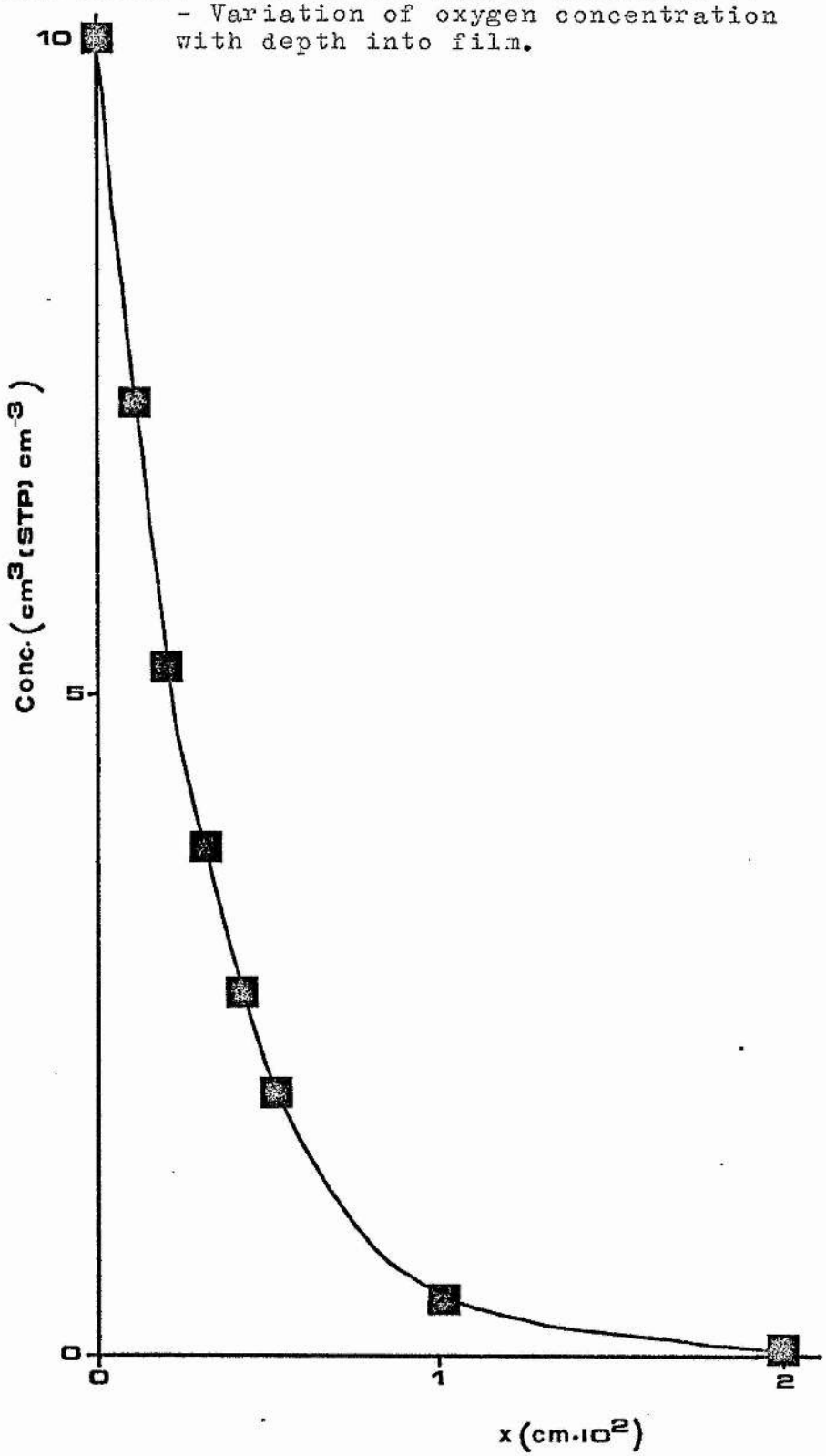


Figure 5.3

Approximate solution for C(x,t) (Equation 7) - Variation of oxygen concentration with depth into film.



renders the first component negligible, and the second part becomes equal to zero, therefore C(x,t) can be approximated by the following equation :-

$$C(x,t) = C_0/2 \exp\{-x\sqrt{k/D}\} [\text{erfC}\{x/2\sqrt{Dt} - \sqrt{kt}\}] \quad 6$$

Due to the inherent properties of error functions, as t increases $\text{erfC}\{x/2\sqrt{Dt} - \sqrt{kt}\}$ rapidly approximates to 2, enabling us to perform a final simplification of equation 2, to produce :-

$$C(x,t) = C_0 \exp\{-x\sqrt{k/D}\} \quad 7$$

Figures 5.2b and 5.2c show how rapidly the above equations converge with the exact solution for C(x,t).

Using equation 7, it was possible to graphically illustrate the concentration gradient in the diffusion controlled region of an oxidising polymer film (Figure 5.3). Combining this with the known concentration present in the diffusion free outer regions of a sample, it is possible to construct a model of the behaviour of $O_2$ concentration within an oxidising sample (Figure 5.4).

Assuming equation 7 to be valid at high values of t, we can now produce greatly simplified equations for a variety of useful parameters important in the investigation of diffusion controlled oxidation of polymer systems :-

$$Q(R) = kC_0 t/\beta \{1 - \exp(-\beta s)\} \quad 8$$

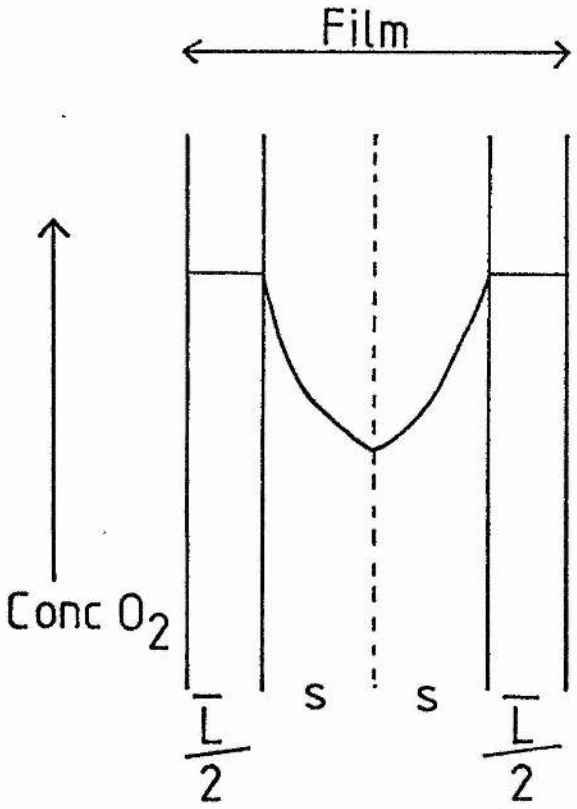
$$Q(T) = C_0/\beta \{1 - \exp(-\beta s)\} \quad 9$$

$$dQ(R)/dt = kC_0/\beta \{1 - \exp(-\beta s)\} \quad 10$$

Where $\beta = k/D$

Figure 5.4

Schematic representation of oxygen concentration in a degrading polymer film.



As we have already emphasised, the above equations apply only to the diffusion controlled zone of the film. It is now necessary to investigate the oxidation kinetics of the diffusion free surface layers of the film, and to devise a way to combine the two into one equation to describe the overall rate behaviour of a polymer film oxidation reaction.

Without diffusion playing a part in the kinetics, the rate expression for oxidation of the diffusion free region of a film is vastly simplified. For a thick film, the rate of oxidation within the diffusion free zone is given by :-

$$dQ(R)/dt = kC_0\bar{L} \qquad 11$$

We have already noted the physical meaning of $\bar{L}$, the limiting thickness, now we must derive a mathematical expression for this quantity in order to be able to include it in the complete rate expression.

We derived an expression for $\bar{L}$ from the equation proposed by Meares [134] to determine the diffusion coefficients of gases in a polymer matrix. Meares statement of this equation is as follows :-

$$Q/Q_\infty = 4/L\{Dt/\pi\}^{1/2} \qquad 12$$

Where Q = amount of gas physically absorbed by a film through both faces at time t; $Q_\infty$ = amount of gas absorbed at equilibrium; and L = film thickness.

An expression for $\bar{L}$ is derived thus :-

Differentiation of 12 w.r.t. time gives :-

$dQ/Q_\infty dt = 1/2\ 4/L\ \{D/\pi t\}^{1/2}$

and substitution of $t^{1/2}$ from 12 gives :-

$dQ/dt = 8DQ_\infty^2/L^2\pi Q$

For the condition $Q = Q_\infty$, this reduces to :-

$dQ/dt = 8DQ_\infty/L^2\pi$

When the rate of chemical consumption equals the rate of physical absorption, the solution is :-

$8DQ_\infty/L^2\pi = kQ_\infty$

$\Rightarrow \bar{L} = \{8D/k\pi\}^{1/2}$ 13

Having derived the above expression for $\bar{L}$, we are now in a position to compile an expression for the rate of oxidation of a polymer film which uses the correct boundary conditions, and takes into account both the diffusion free, and diffusion controlled kinetics which affect this rate. The overall rate is a combination of the rate in the <u>total</u> diffusion controlled zone, and the rate in the diffusion free surface layers. Combining the equations derived above, we obtain the solution :-

$dQ(R)/dt = kC_0\bar{L} + 2kC_0/\beta\ \{1 - \exp(-\beta s)\}$ 14

In utilising this expression, it is important to remember that we have split the film thickness into separate regions, and that this must be taken into account when plotting data which involves variation of the film thickness. Overall film thickness will be equal to $\bar{L} + 2s$.

### 5:2:5 Induction Time

Plots of reaction parameter (carbonyl index, optical density, oxygen uptake) vs. time for both photochemical and thermal autoxidation of polyolefins show an initial period in which no reaction appears to take place [1], followed by an approximately straight line relationship between the parameter and time. This time period of seeming non-activity is refered to as the induction time of the reaction and is a function of the film thickness, rate of diffusion of reacting $O_2$, and the rate constant of the oxygen consuming reaction, i.e. $t_{ind} = f(L, D, k)$.

Some authors consider this period to be the time required to accumulate a "critical concentration of hydroperoxides" [130]. These are then responsible for the rapid oxidation which follows the induction period. There is another way to consider this phenomenon, however. Having already explained the need to consider two distinct zones in a polymer film, it may be considered that the induction time is due to the establishment of a physical equilibrium between these two, and not to a chemical induction period.

Consider the mass balance equation for the diffusion controlled zone (Equation 5); this may be written as $Q(A) = Q(R) + Q(T) - Q(0)$. For the entire film it is necessary to include a term denoting the amount of oxygen in the diffusion free zone; this is shown in equation 15, where $1/2\ Q(H)$ is the amount of $O_2$ present in the diffusion free zone at one surface of the film :-

$$Q(A') = Q(R) + Q(T) + 1/2\ Q(H) - Q(0) \qquad 15$$

Let the amount of gas absorbed from external sources equal zero;

i.e. $t_{ind}$ is equivalent to that period of time during which the reaction within the film is self-sustaining in oxygen. Applying this equation 15 becomes, solving for time, equation 16 :-

$$t_{ind} = 1/k\left[\frac{\beta s - \{1 - \exp(-\beta s)\}}{\beta L/2 + \{1 - \exp(-\beta s)\}}\right] \qquad 16$$

It should be noted that it is not possible to derive an equation for the induction time from the *exact* solutions, because of the presence of integral terms.

5:2:6 Comparison with Experimental Results

In order to determine the applicability of our theory, two investigations were chosen as examples; the data of Billingham and Walker [132] for the thermal oxidation of poly(methylpentene), and that of Chien and Boss [130] for the thermal oxidation of thick films of poly(propylene).

The value of the initial $O_2$ concentration, $C_0$, used in both cases was that of $2.7\times10^{-2}$ $cm^3(STP)cm^{-3}$ estimated by Billingham and Walker [132]. The value of the rate constant, k, was calculated from the early part of the rate vs. thickness plot for both cases, assuming the straight line relationship Rate = $kC_0L$ to apply. Values of 0.448 $s^{-1}$, and 0.965 $s^{-1}$ were obtained for Billingham and Walker [132] and Chien and Boss [130] respectively.

By varying the value of the diffusion coefficient, D, in each case, and using equation 14, excellent correlations between the theoretical plots and experimental data were found. Best fits were obtained for $D = 5.5\times10^{-6}$ $cm^2$ $s^{-1}$ in the case of

Figure 5.5

Correlation of theoretical (Eqn.14) solution of rate of oxidation vs. film thickness and experimental results of Billingham and Walker [132].

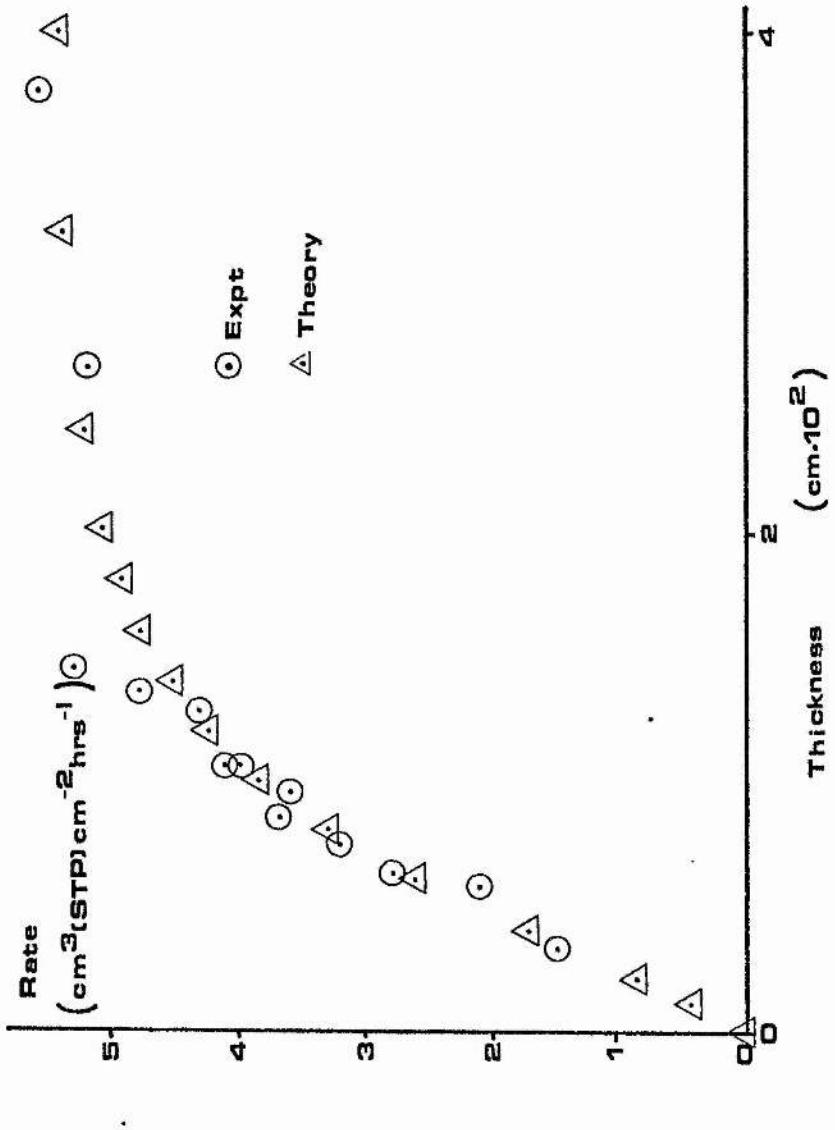


Figure 5.6

Correlation of theoretical (Eqn.14) solution of rate of oxidation vs. film thickness and experimental results of Chien and Boss [130].

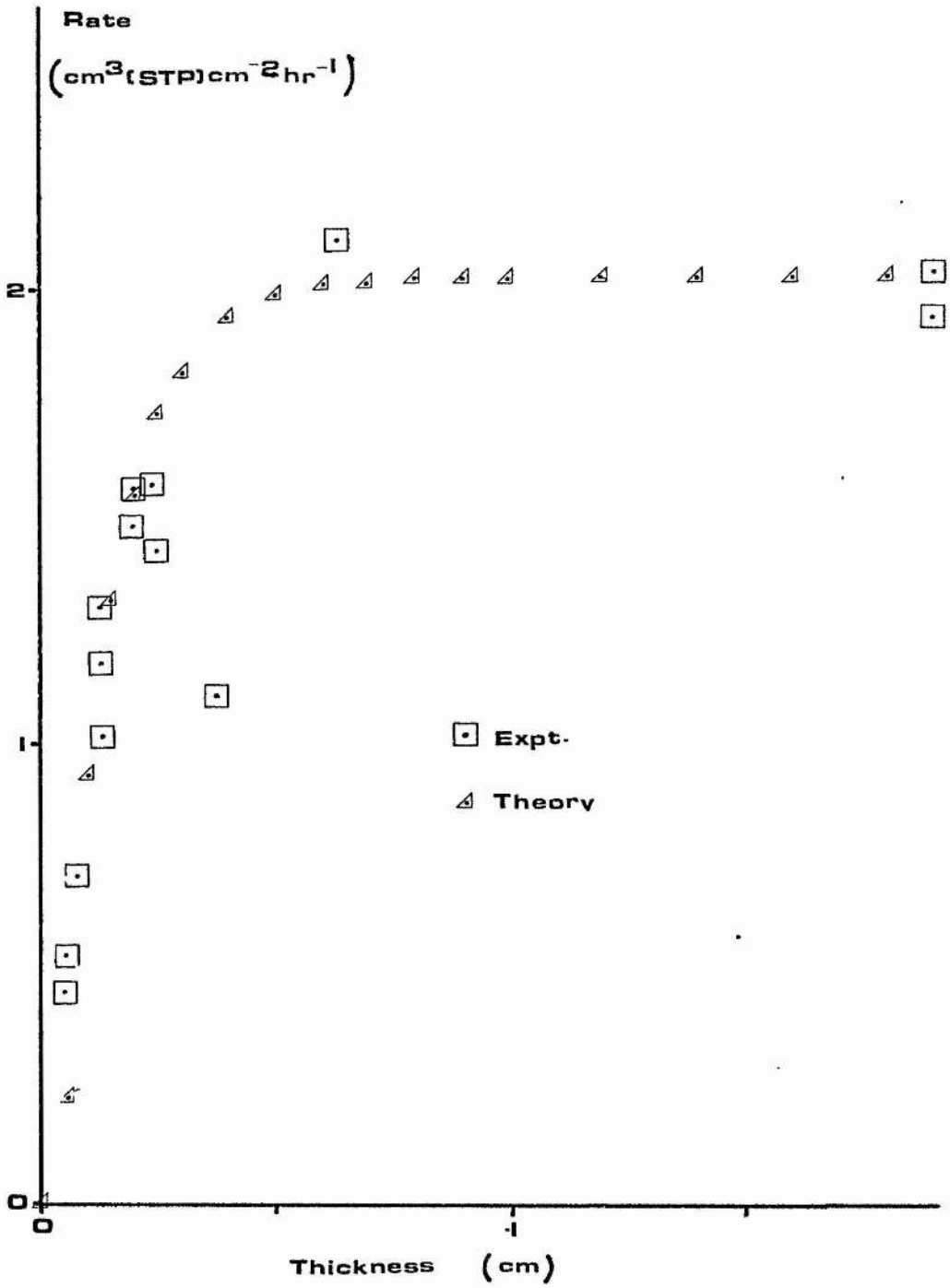
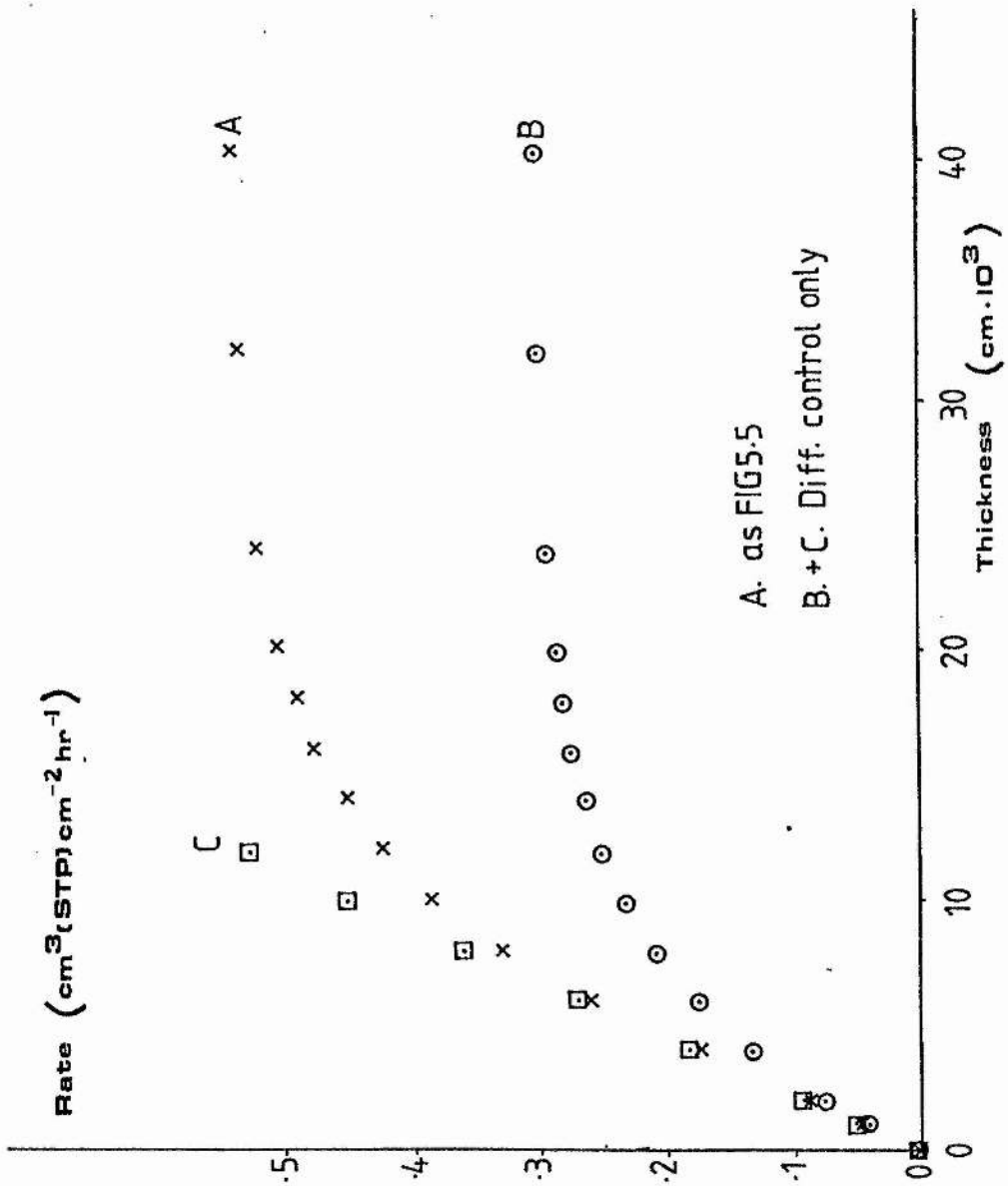


Figure 5.7

Comparison of equation 14 with theoretical solutions assuming diffusion control from the sample surface.



Billingham and Walker, and $D = 3.5 \times 10^{-5}$ $cm^2$ $s^{-1}$ in the case of Chien and Boss (Figures 5.5 and 5.6). These values, considering the assumptions made for initial $O_2$ concentration and in the mathematics, are reasonable estimates of the diffusion coefficient of oxygen in a polymer system.

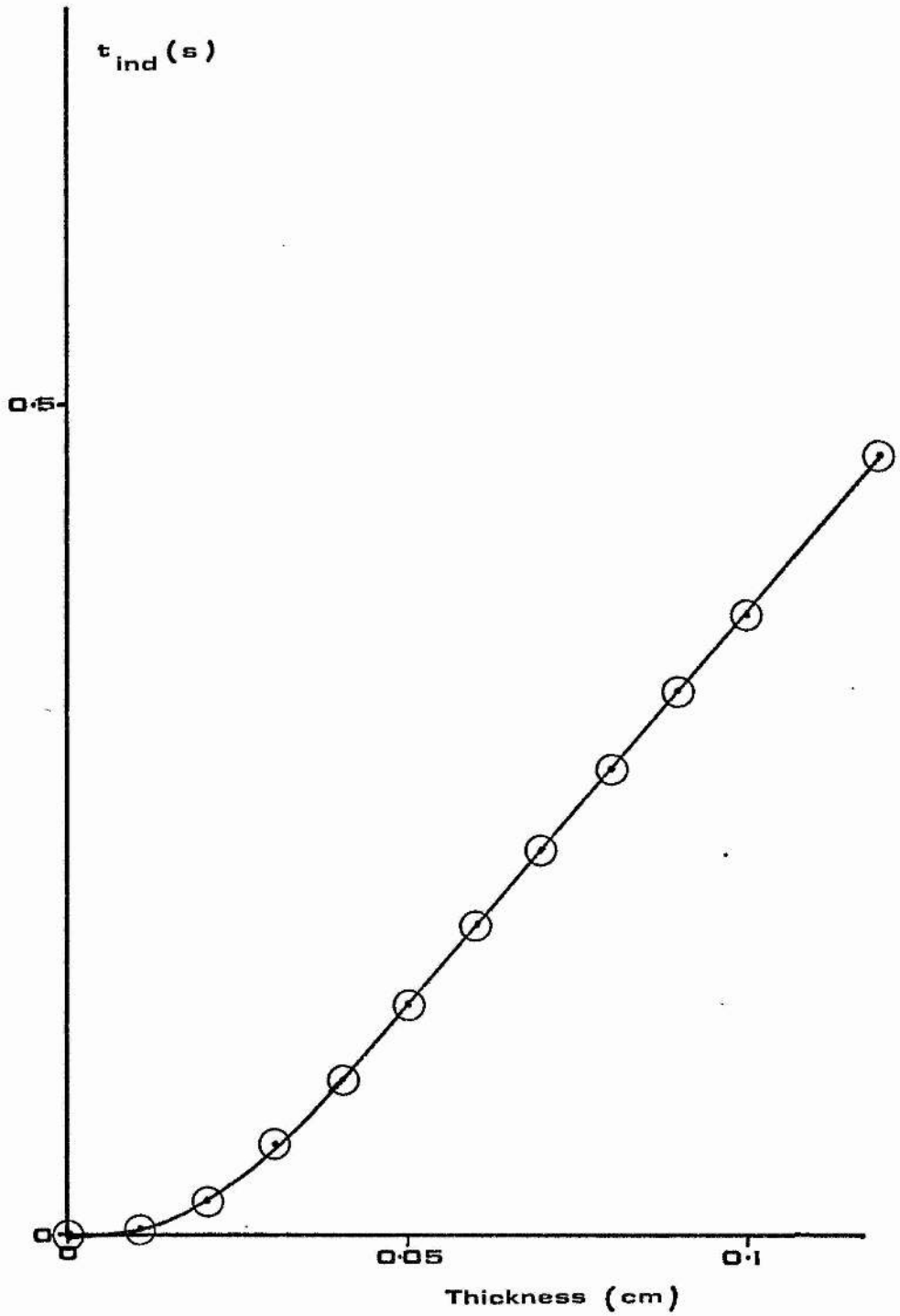
The above comparison with experimental data shows that the inclusion of diffusion free and diffusion controlled terms produces a rate equation which is a good model of an oxidising polymer system. A further test was to use equation 10, i.e. assuming diffusion control from the surface, and to test whether this could be made to fit the curve found experimentally. As is shown in Figure 5.7, it was not possible, using this version of the oxidation kinetics, to produce a reasonable fit to experimental data. This is further evidence of the veracity of our model.

Using the theoretical best fit data for the results of Chien and Boss [130], a plot of $t_{ind}$ vs. film thickness was prepared. As can be seen from Figure 5.8, after an initial phase of non-linearity, due to the dominance of diffusion free kinetics, there exists a direct proportionality between induction time and film thickness.

From the above evidence, it would appear tnat the model of oxidation of polymers described in this section correlates well with the actual chemical and physical processes involved. Equation 14 appears to adequately combine both diffusion controlled and diffusion free kinetics in such a way as to be a useful model of the oxidation behaviour of polymer films of all

Figure 5.8

Variation of induction time with film thickness (Eqn.16).



thicknesses.

## 6. SUMMARY AND CONCLUSIONS

Having investigated some of the various proposed mechanisms for the excellent photostabilising action of HALS in polyolefins, it is the purpose of this chapter to compare the results obtained, and preliminary conclusions reached, in each of the experimental sections, and to attempt to provide a clearer picture of the mechanism involved in the photostabilisation of polyolefins by HALS. Theoretical investigation of the effects of $O_2$ diffusion on the oxidation of polymers has shown this to be a critical factor, and we will here apply this result to the investigation of HALS stabilisation mechanisms, and show how the derived equations can be used to test some of the suggested mechanisms for HALS action.

### 6:1 Screening of Detrimental Light.

For the parent amines this has been shown to be of little practical importance, due to their very low extinction coefficients in the visible and near - ultra-violet regions of the spectrum. The nitroxide derivatives we have already noted to be highly coloured (orange - red) and this leads to high extinction coefficients in the visible region, which could lead to photoreaction of the substrate. The nitroxides, in a commercial stabilising situation would be present in very low concentrations in any case. It is obvious that screening does not contribute to the stabilising ability of HALS.

### 6:2 Quenching of EES.

The experiments carried out in Section 4:1 on aromatic and carbonyl EES in polymer matrix pointed out that, even in fairly high ratios of stabiliser to additive, there is no appreciable quenching of triplet excited states involved. Comparison of the singlet quenching ability of HALS with that of non-hindered amines, in the case of aromatic singlets in fluid solution, shows little difference between the two types, both in general being poor quenchers of EES; this is contrary to the results of Heller and Blatmann [31]. Our results show that, in order for any amine to be an effective quencher of singlet EES, it is necessary that it exhibits a low ionization potential (IP), since these compounds quench excited states by an excited state charge transfer mechanism [31]. Few, if any, of the commercial stabilisers will have a sufficiently low IP to act as singlet EES quenchers by this means.

Experiments carried out to test the quenching ability of nitroxides in the case of excited states of anthracene and tetracene would seem to suggest that the radicals synthesised from commercial HALS have a weak capability of quenching singlet oxygen, due to the paramagnetic nature of the N - O. group - this is in keeping with results presented by other authors [67,68]. In polyolefins, the role, if any, of singlet oxygen in photo-oxidation is not clear, and it would appear that the role of nitroxides as quenchers of this species would not be a significant factor in the photostabilising ability of HALS. In the case of polydienes, where singlet oxygen is thought to be of importance in the photo-oxidation mechanism, published results [48] suggest that quenching of singlet oxygen by HALS is not a

viable stabilisation mechanism.

6:3 Non-radical Decomposition of Hydroperoxide.

As we have already noted, in order for ROOH to be actively decomposed by HALS, it is necessary for the two species to be in close proximity. Due to the low concentration of both species and the diffusion problems discussed in Section 5:1, such a situation on a purely random distribution basis is unlikely. Some authors [55,56] have suggested that association formation between HALS and ROOH might provide a pathway whereby this stabilisation mechanism might become a significant factor.

Following this line of enquiry, the results which we obtained (Section 4:2) clearly demonstated that the percentage of available ROOH and HALS which would actually take part in any such association would be extremely low. The results from IR spectroscopy show very low association constants for such complexes, even in fluid solution. NMR spectra do show an extremely large effect on the hydroperoxy proton chemical shift on addition of HALS, but this is essentially a qualitative observation, and does not in any way invalidate the conclusions reached from the IR evidence. The large NMR chemical shifts exhibited in these experiments can be explained by the extreme sensitivity of the hydroperoxy proton to changes in its environment [113].

The data presented in Section 4:2 is conclusive evidence that HALS and ROOH do not form appreciable percentages of associated species; this makes any stabilisation mechanism involving the decomposition of hydroperoxides by either HALS or

their nitroxide derivatives unlikely as an explanation of the photostabilising ability of these compounds.

6:4 Interception of Photo-oxidation Products.

In this case, the stabiliser is being required to deal with one or more of a series of photoproducts produced in the later stages of reaction. Two important classes of chromophore have been investigated - the hydroperoxides, and the carbonyls.

For hydroperoxides the same observations apply as noted above, except that we may now expect a higher concentration of hydroperoxide. Hence, it might be expected, from a purely random distibution of ROOH and HALS that some conversion of HALS to nitroxide may now occur, and this can account for the low steady-state concentration (c. 1%) of nitroxide found in photodegraded sample of poly(propylene) stabilised by HALS. This reaction will not be an effective stabilisation mechanism in its own right, since the vast majority of hydroperoxy groups will be unaffected by it, and able to take part in the ongoing autoxidation reaction.

We have already noted the suggestion [80] that HALS might interact with unsaturated ketone photo-oxidation products, in order to prevent their isomerisation to more photochemically active species, but this pathway has a number of problems associated with it. The mechanism proposed [80] involves very high speed proton transfer from the HALS to the ketone, which is not a likely occurance in a polymer matrix, and of course is not possible in the case of the tertiary amine stabilisers. The concentration of such "specialised" chromophores is also liable

to be small, and they are not consumed in the reaction with HALS but remain intact and could thus possibly still contribute to the degradation through energy transfer mechanisms.

### 6:5 Stabiliser Transformation.

The fact of HALS transformation to other derivatives, notably stable nitroxide radicals, is well documented [51,52,53]; the further effect of such species on the autoxidation behaviour of polyolefins is less well defined. There is ample evidence for the formation of a low (c. 1% of original stabiliser concentration) steady-state population of nitroxide radicals during photo-oxidation of poly(propylene) containing secondary HALS [51]. Some authors also detect hydroxylamines [60,62] and hydroxylamine ethers [52]. In the case of tertiary HALS we have shown, in a series of long term experiments, that the N - methyl substituted stabiliser Tinuvin 292 is capable of forming a very low concentration of radical species in the presence of massive excess of ROOH, although very much lower than the concentration noted for Tinuvin 770. In the case of Tinuvin 622, a tertiary HALS which has its nitrogen as essentially part of the polymer backbone, no formation of radical species was noted, even over a period of several weeks; yet Tinuvin 622 is a highly effective stabiliser. Similar experiments by Jensen et al [66] suggest that T292 reacts with oxygen centred radicals to produce T770 which then reacts with ROOH to produce the radicals, although here again we encounter the problem of diffusion of the reacting species in a polymer matrix. The inefficient nature of both reactions is reflected in the low concentration of radicals noted even for T770, and the vast differance in concentration noted between the two stabilisers, both being monitored over a period

of weeks.

These observations, and their correlation with work by other authors tend to suggest the same conclusions noted in other sections of this chapter, i.e. that transformation products of HALS, although capable in theory of performing a variety of stabilising functions, are too inefficient, and available in too small a quantity, to fully explain the photostabilising ability of commercial HALS.

## 6:6 Radical Scavenging.

As explained in Section 2:3, there is a great deal of controversy surrounding this particular stabilisation mechanism. Authors have cited nitroxyls, hydroxylamines, and hydroxylamine ethers, or all three as radical trapping species in the photostabilisation of poly(propylene) [52,62,84,88,89]. Let us now consider this more closely.

In photodegradation of a polyolefin, there are two types of radical involved in the autoxidation cycle - alkyl radicals, R., associated with the initiating step, and oxygen centered radicals, the hydroperoxy, ROO., and alkoxy RO., species , associated with propogation and chain branching respectively. As it would be ideal to capture, or render harmless, the initiating radical, any scavenging of R. would be an important stabilising process. Nitroxyl radicals are suggested as alkyl radical scavengers, but there are two important problems with this hypothesis :-

a) We have already shown that the nitroxyl radicals do not associate with hydroperoxide to any appreciable extent; Table 4.F shows that nitroxides are even less likely to form associations with ROOH than their parent amines, and therewith the oxidising domain of the polymer, therefore there is no advantageous proximity of the radical trap to a potential radical site. The size of commercial HALS makes it unlikely that they can diffuse towards a radical site within the timescale required to prevent reaction between R. and $O_2$.

b) A situation whereby the nitroxyl might react with R. within the lifetime of the free alkyl radical would arise if there were a severely depleted oxygen supply in the immediate vicinity, but in the case of thin films and fibres, the mathematical model set out in Section 5:2 suggests that, assuming reasonable values for D and k, there will be no diffusion control of oxidation, i.e. no oxygen depletion to assist a nitroxyl - alkyl radical reaction.

The scavenging of alkoxy and/or peroxy radicals by hydroxylamines and hydroxylamine ethers is another suggested mechanism, and this would in fact be vital for the regeneration of nitroxyl radicals [53,62], but again the restricted mobility and low concentration of these species in a polymer environment will keep this process to too low a level to contribute significantly to the excellent photostabilisation properties of HALS.

Thus the cycle of reactions between polymeric radicals and HALS derivatives can theoretically take place, but it would appear that the low levels detected of nitroxides and hydroxylamines suggest that this is of minor importance to the overall efficiency of the photostabilisation mechanism associated with HALS. Moreover, some literature reports indicate that high stability of a sample is not necessarily connected with a high concentration of nitroxyl radicals [48,90], plus results using Tinuvin 622 noted in the previous section show that radical species are not necessarily required at all in order for a commercial HALS to be an effective polyolefin photostabiliser.

### 6:7 Transition Metal Complexation.

Enhancement of oxidation of polymers by transition metal compounds has been suspected for some time, but little has been done to investigate the extent to which this reaction occurs, or the mechanism(s) involved. Early work on metal catalysis of autoxidation tended to concentrate on the effects of metal impurities in liquid hydrocarbons, particularly the important studies of Uri et al [26], although some investigations were carried out on low MW polyolefins by Kresta et al [135]. Both these authors established two important points concerning the reaction - a) Only a very low concentration of transition metal ion is required to substantially catalyse the reaction, b) In higher concentrations, the metal ions compete successfully for alkoxy and peroxy radicals, and act as chain terminators.

A model reaction between $H_2O_2$ and transition metal species [27] indicated that photolysis of the peroxide would not occur unless a low level of transition metal ion was present. Complimentary to this, Tkac et al [136] have shown that catalysis of poly(propylene) oxidation by Co(II) does not proceed except in the presence of hydroperoxide species. More recently, Allen et al [137] have confirmed the detrimental effect of residual transition metal catalysts on the photochemical and thermal stability of poly(propylene).

The above observations can be explained by adopting the theory of Black [28], that the so-called metal catalysed autoxidation of hydrocarbons is due to initiation by a metal - hydroperoxide complex. The initiation of autoxidation through this mechanism is illustrated below, using iron as an example of a transition metal of variable valence.

$$Fe^{2+} + ROOH \rightleftharpoons (ROOHFe)^{2+}$$

$$(ROOHFe)^{2+} \longrightarrow RO. + Fe^{3+} + OH^-$$

$$Fe^{3+} + ROOH \rightleftharpoons (ROOHFe)^{3+}$$

$$(ROOHFe)^{3+} \longrightarrow ROO. + Fe^{2+} + H^+$$

With the above observations in mind, it can readily be seen that the ability shown by HALS, in Section 4:3, to complex with transition metals is crucial to their ability to act as excellent photostabilisers. The fact that such a wide range of transition metals are complexed by HALS is noteworthy, in that many different elements are liable to be present in a commercial film or fibre, either from deliberate addition of pigments, stabilisers, etc., or as trace impurities from catalysts or

processing. Richters has shown [5] that poly(propylene) film may contain as many as 8 different transition metals, in amounts ranging from 0.1 - 25 ppm. Our own analyses of HALS containing polymer films show that Fe is present in concentrations equivalent to $5 \times 10^{-6}$ - $10^{-5}$ Molar, i.e. a level which would be capable of substantially accelerating autoxidation of a liquid hydrocarbon [26].

Inferring from solution phase results the behaviour of an additive or impurity in polymer matrix has always to be done with caution. Our examination of impurity mobility in Section 5:1 has, however, put forward a good case for metal ions being fairly small, highly mobile species, capable of diffusing through a polymer matrix, since the main ligands appear to be oxygen and/or small organic species [135]. Initial processing of the polymer into a finished article will, as already indicated, present opportunities for the contamination of the feedstock by metal impurities from machinery. These metal species will be picked up on the surface of the film, where they are likely to encounter stabiliser species which, being only partially soluble in the polymer, will tend to migrate slowly there. This, in conjunction with the high temperatures used in the processing of most polyolefins, creates an ideal situation as regards mobility of metal containing species. Once the film or fibre is in use, the ROOH which is considered to be created at this stage [2] and the $M^{n+}$ are available to initiate further degradation under thermal or photochemical oxidation conditions. It has been noted [5] that metal impurities can rapidly diffuse into the bulk of a poly(propylene) sample from the surface, and, particularly relevent to our hypothesis, Clark and Peeling [138] have observed

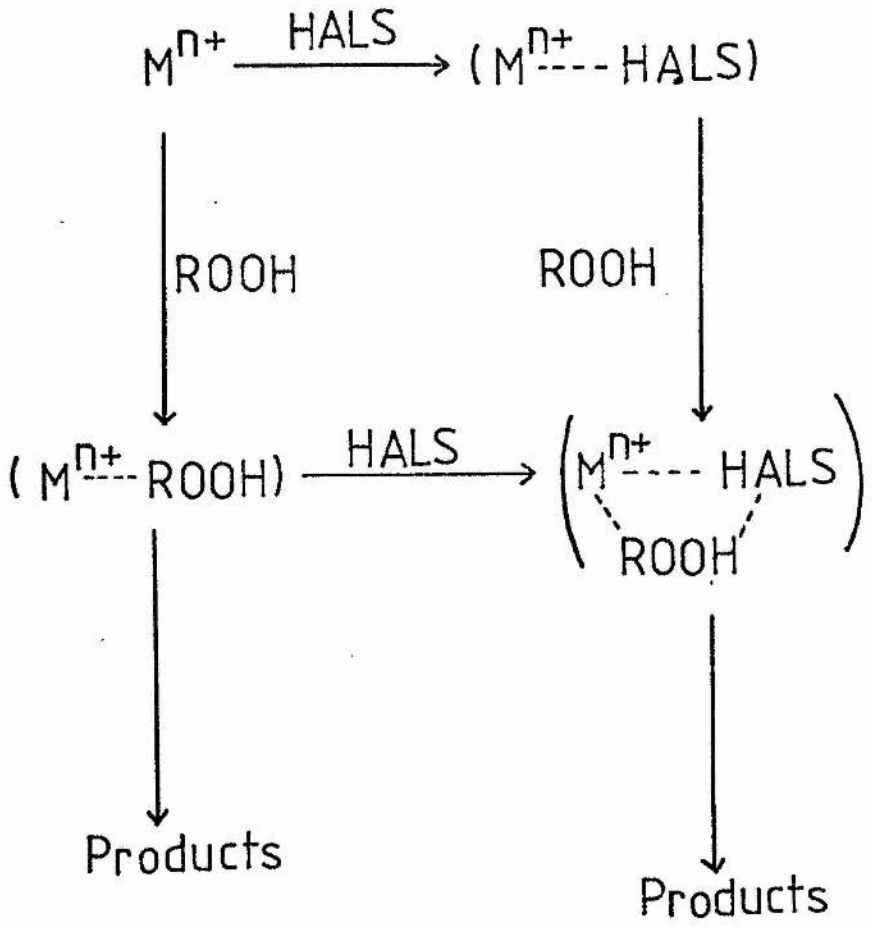
that, in a thin, metal free, surface layer, no oxidation products appear in oxidised poly(ethylene). The high rate of reaction of HALS and $M^{n+}$ in solution, and the mobility of the metal species in polymer matrix, will combine to provide a useful stabilisation mechanism.

Experiments carried out in Section 4:3 on the ability of the HALS derived nitroxide radicals to complex with transition metal species have shown that this is not an important mechanism. While nitroxides show some complexing ability with selected species (e.g. Fe(II)), the reaction is not as efficient as for the parent HALS, and not nearly so general throughout the transition series. An explanation of this differance is not easy to formulate, but must be connected with the paramagnetic nature of the radicals, and hence possibly with the differing electronic configurations of the various transition metal ions. The low level of HALS converted to nitroxides in a degrading polymer system will not noticably affect the efficiency of the HALS additive as a metal complexing stabiliser.

A general scheme of reactions it would be possible for $M^{n+}$ to undergo can be envisaged as shown in Figure 6.1. For this scheme to be successful as a polymer stabilising mechanism, the strength of complex formation between HALS and $M^{n+}$ must be greater than that between ROOH and $M^{n+}$. We have shown the reaction between hindered amines and metal ions to be fast and almost complete; qualitative comparisons with EDTA complexes of iron and cobalt show that HALS are as good, if not better, complexing agents. Richardson [139] has shown that a cobalt complex of EDTA is unable to react with ROOH. These results

Figure 6.1

Reaction scheme for interaction of HALS and transition metal ions.



suggest that the complexing ability of HALS towards transition metals is far greater than that of ROOH, hence reactions 1 and 4 in Figure 6.1 will predominate.

The stoichiometry of the reaction between HALS and $M^{n+}$ is difficult to establish. Atomic absorption spectroscopy was unsuccessful due to interference from other trace elements in the system, and microanalysis gave ambiguous results. Di- and poly-amines are known to form a variety of "wraparound" complexes with transition metals, of varied conformation and stoichiometry [140] - the various in vivo complexes such as haemoglobin and chlorophyll are prime examples of this - so that this ambiguity in ratios is perhaps understandable.

The observation of apparent changes in oxidation state involved in the reactions between lower oxidation state transition metals and HALS are interesting. Investigations showed that triethylamine could produce a similar effect on aqueous solutions of Fe(II). The key to this reaction is the presence of $O_2$ and $H_2O$ plus the very high basicity of the HALS (pKa = 10 - 14). In our experiments, water is present either as part of the solvent system, or as an impurity in the acetone; while $O_2$ will be present dissolved in the solvent. These circumstances would account for the interconversion of the transition metal oxidation states; the rate of this process will depend on the relative stabilities of the oxidation states of a particular transition metal. It will also be noted that, in a polyolefin undergoing oxidation, water is a product of the reaction, being created during H - abstraction by .OH radicals, and will also diffuse into the sample from the atmosphere.

The proposed photostabilisation of polyolefins by complexing of trace transition metals may be presented as a series of complimentary processes :-

1) Reduction of light absorption by transition metal ions, thereby preventing the accumulation of energy necessary to initiate the homolytic scission of the $M^{n+}$ - ROOH complex; also breaking up any energy transfer processes which might occur between adjacent metal ions, or between $M^{n+}$ and other acceptor species.

2) Prevention of formation, or break-up, of $M^{n+}$ - ROOH initiating complexes.

3) Creation of optimum conditions for disruption of any redox equilibrium processes involving hydroperoxides and transition metal ions of variable valence.

4) Drastic reduction in mobility and availability of $M^{n+}$.

5) Complexes appear to be insoluble in organic media, therefore there will be an increase in the heterogeneous nature of chemical processes, and a consequent decrease in reaction rates.

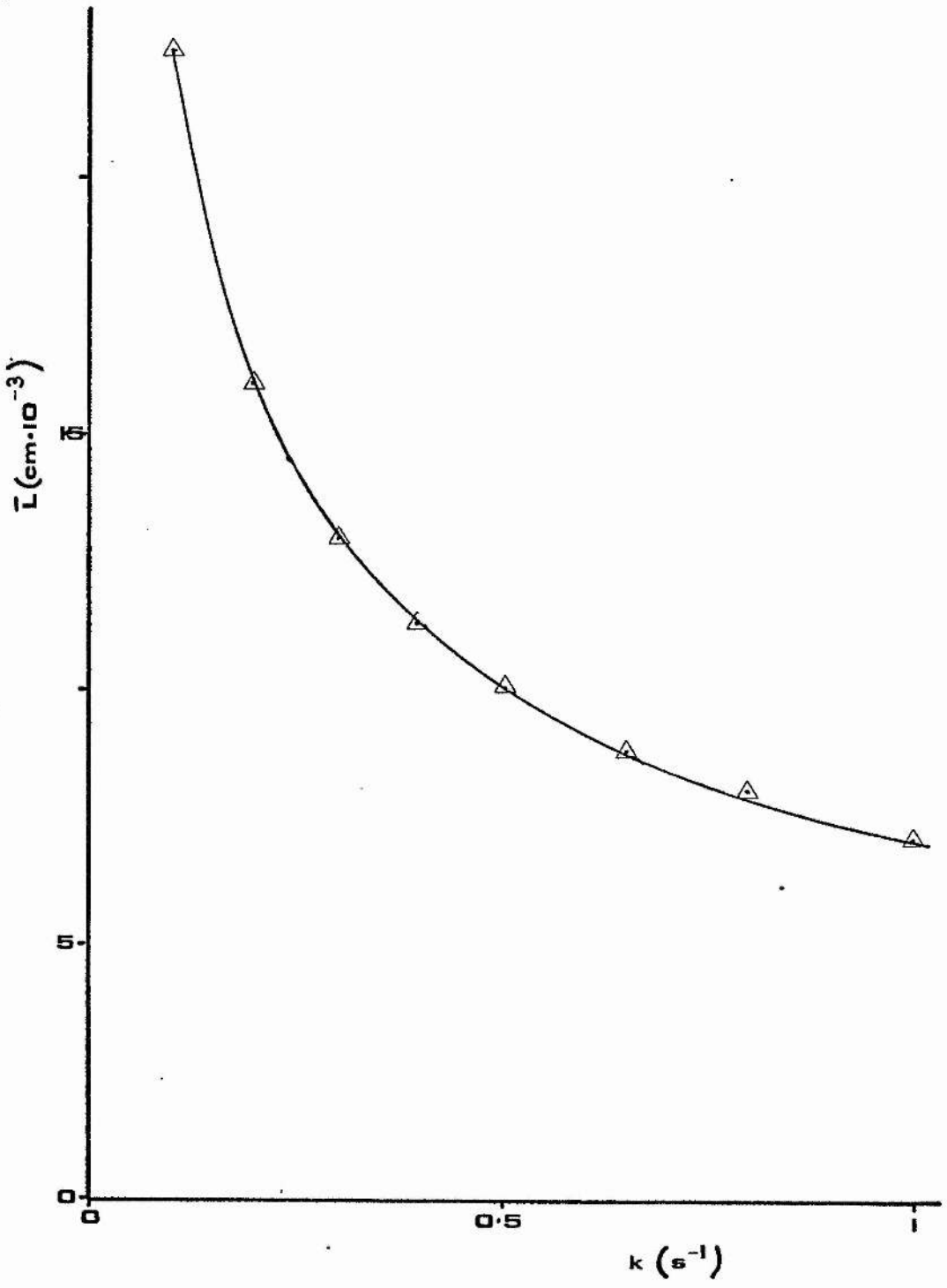
6:8 Effects of Oxygen Diffusion.

The mathematical model developed in Section 5:2 is, we believe, the best approximation developed so far, within the assumptions made, to explain the oxidation behaviour of polyolefin films. Incorporation into the final equation of kinetic expressions dealing with both diffusion free and diffusion controlled regions of the sample gives a model which is in excellent agreement with the experimental results for variation of rate of oxidation with sample thickness (Figures 5.5 and 5.6). The correctness of the model incorporating both types of kinetic behaviour is illustrated dramatically in Figure 5.8, which shows that, in order to match experimental results, both sections of equation 14 are required. Boundary conditions used also take into account the equilibrium concentration of oxygen present in a polymer film, whereas most previous models assume zero concentration of $O_2$ within the film at time zero [129,130,131,132].

Further proof of the close correlation between our model and experiment can be seen when a comparison is made between the schematic diagram of $O_2$ concentration within a polymer film during oxidation (Figure 5.4) and the results of Davis et al [141] for the concentration of carbonyl groups across a degraded film. The literature results show a constant concentration of carbonyl for some depth into both faces of the sample, which matches the profile type shown in Figure 5.4, therefore the explanation is obvious - this distribution of carbonyl groups is caused by there being two distinct kinetic domains within the film, i.e. the presence of diffusion free zones at both faces of the sample, and a diffusion controlled zone within the sample.

Figure 6.2

Variation of limiting thickness with oxidation rate constant (Eqn.13).



The consequences of the model to the stabilisation behaviour of HALS in a polyolefin matrix must now be examined. Proposed [84] mechanisms of stabilisation, such as radical scavenging, will require a substantial local reduction in oxygen concentration, to prevent the rapid consumption of alkyl radicals by oxygen in the autoxidation cycle. Figure 6.2, which shows a plot of limiting thickness vs. rate constant of the oxidation reaction, graphically illustrates that, in thin polymer films (0.02 - 0.1 mm), this situation will not arise. In the case of a dense polyolefin with a high diffusion coefficient of $O_2$, there may occur a thin layer towards the centre of the film where the oxygen supply is limited, and here, as in the case of thick samples, diffusion of oxygen to the reaction site may prove to be the rate determining step, particularly in thermal degradation. In photodegradation, however, the oxidation is confined to the upper levels of the film [142] due to rapid loss of light energy on penetration of the sample, thus diffusion control is less likely to be a significant factor in this case, except under high energy and/or UV testing. Without the low $O_2$ levels, alkyl radicals will rapidly react with oxygen before the bulky nitroxide radical derivitives of HALS can attack, therefore radical scavenging will not be a viable stabilisation mechanism.

## REFERENCES


1. B.Ranby, and J.F.Rabek, "Photodegradation, Photo-oxidation and Photostabilisation of Polymers", Wiley-Interscience, London, (1975)

2. D.J.Carlsson, and D.M.Wiles, J. Macromol. Sci., Rev. Macromol. Chem., C14, 65 (1976)

3. O.Cicchetti, and F.Gratini, Eur. Polym. J., 8, 561 (1972)

4. H.C.Ng, and J.E.Guillet, Macromol., 11, 937 (1978)

5. P.Richters, Macromol., 3, 262 (1970)

6. N.S.Allen, R.B.Cundall, M.W.Jones, and J.F.McKellar, Chem. Ind., 110 (1976)

7. J.Lacoste, R.Arnaud, and J.Lemaire, Compt. Rend., 295, 1087 (1982)

8. H.J.Heller, Eur. Polym. J. Suppl., 105 (1969)

9. Ref. 1, p.279

10. G.Gueskens, and C.David, Pure Appl. Chem., 49, 479 (1977)

11. N.J.Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, (1978) p.296

12. T.Forster, Disc. Farad. Soc., 27, 7 (1959)

13. D.L.Dexter, J. Chem. Phys., 21, 836 (1953)

14. S.W.Beavan, and D.Phillips, J. Photochem., 3, 349 (1974/75)

15. D.J.Carlsson, and D.M.Wiles, Macromol., 5, 689 (1972)

16. D.J.Carlsson, and D.M.Wiles, Macromol., 7, 259 (1974)

17. P.J.Briggs, and J.F.McKellar, J. Appl. Polym. Sci., 12, 1825 (1968)

18. A.P.Pivoverov, Y.A.Ershov, and A.F.Lukovnikov, Sov.Plasti., 10, 11 (1967)

19. D.J.Carlsson, and D.M.Wiles, J. Polym. Sci. Polym Chem. Ed.,

12, 2217 (1974)

20. D.C.Mellor, A.B.Moir, and G.Scott, Eur. Polym. J., 9, 219 (1973)

21. J.D.Holdsworth, G.Scott, and D.Williams, J. Chem. Soc., 4692 (1964)

22. A.Negishi, Y.Ogiwara, and Z.Osawa, J. Appl. Polym. Sci., 22, 2953 (1978)

23. J.Charlambous, and M.J.Frazer, J. Chem. Soc. A, 2361 (1964)

24. A.G.Akhmadullina, N.A.Mukmeneva, and P.A.Kirpichnikov, Plast. Massy., 14 (1971)

25. J.Kresta, L.Ambroz, and K.Obucova, Chem. Prum., 17, 25 (1967) [CA66:116219v]

26. N.Uri, Israel J. Chem., 8, 125 (1970)

27. S.Lunak, and J.Veprek-Siska, Z. Naturforsch. B, 36, 654 (1981)

28. J.F.Black, J. Am. Chem. Soc., 100, 527 (1978)

29. D.J.Carlsson, A.Garton, and D.M.Wiles, Dev. Polym. Stab., 1, 219 (1979)

30. J.C.W.Chien, In "Degradation and Stabilisation of Polymers", G.Geuskens Ed., Applied Science, London, (1977) p.205

31. H.J.Heller, and H.R.Blattmann, Pure Appl. Chem., 36, 141 (1973)

32. E.Niki, C.Decker, and F.R.Mayo, J. Polym. Sci. Polym. Chem. Ed., 11, 2813 (1973)

33. C.Decker, and F.R.Mayo, J. Polym. Sci. Polym. Chem. Ed., 11, 2847 (1973)

34. K.Murayama, S.Marimura, and T.Yoshioka, Bull. Chem. Soc. Japan, 42, 1640 (1969)

35. J.L.Brockenshire, J.R.Roberts, and K.U.Ingold, J. Am. Chem. Soc., 94, 7040 (1972)

36. Ref. 1 p.413

37. H.P.Franck, and H.Lehner, J. Polym. Sci. C, 31, 193 (1970)

38. W.L.Hawkins, W.Matreyek, and F.H.Winslow, J. Polym. Sci., 41, 1 (1959)

39. N.C.Billingham, and P.D.Calvert, In "Developments in Polymer Stabilisation " Vol.3, Ed. G.Scott, Applied Science, New York, (1980) p.139

40.P.D.Calvert, and N.C.Billingham, J. Appl. Polym. Sci., 24, 357 (1979)

41. E.G.Rozantsev, and V.D.Scholle, Synthesis, 414 (1971)

42. Ref. 1, p.97

43. Brit. Pat. 130799 (26.11.65)

44. Brit. Pat. 196244 (22.6.67)

45. P.P.Klemchuk, Advances in the Stabilisation and Controlled Degradation of Polymers, 2nd Intern. Conf., Luzerne, (1980)

46. Chimassorb 944, Preliminary Product Information, Ciba-Giegy Ltd., (1979)

47. S.Wu, G.Dui, and L.Liu, Kao Fen Tzu T'uang Hsun, 234 (1981) [CA96:7479d]

48. Y.Y.Yang, J.Lucki, J.F.Rabek, and B.Ranby, Polym. Photochem., 3, 49 (1983)

49. Tinuvin 622, Preliminary Product Information, Ciba-Giegy Ltd., (1978)

50. Tinuvin 765, Preliminary Product Information, Ciba-Giegy Ltd., (1981)

51. D.J.Carlsson, D.W.Grattan, T.Suprunchuk, and D.M.Wiles, J. Appl. Polym. Sci., 22, 2217 (1978)

52. D.K.C.Hodgeman, J. Polym. Sci. Polym. Chem. Ed., 18, 533 (1980)

53. D.K.C.Hodgeman, J. Polym. Sci. Polym. Chem. Ed., 19, 807 (1981)

54. K.B.Chakraborty, and G.Scott, Chem. Ind., 237 (1978)

55. J.Sedlar, J.Petruj, J.Pac, and M.Navratil, Polymer, 21, 5 (1980)

56. J.Sedlar, J.Marchal, and J.Petruj, Polym. Photochem, 2, 175 (1982)

57. D.W.Grattan, A.H.Reddoch, D.J.Carlsson, and D.M.Wiles, J. Polym. Sci. Polym. Lett. Ed., 16, 143 (1978)

58. D.J.Carlsson, K.H.Chan, and D.M.Wiles, In "Photodegradation and Photostabilisation of Coatings.", A.C.S., (1981) p.51

59. Y.B.Shilov, and Y.T.Denisov, Vysokomol. Soedin. A, 16, 2313 (1974)

60. K.Chakraborty, and G.Scott, Polymer, 21, 252 (1980)

61. D.W.Grattan, D.J.Carlsson, J.A.Howard, and D.M.Wiles, Can. J. Chem., 57, 2834 (1979)

62. R.Bagheri, K.B.Chakraborty, and G.Scott, Polym. Deg. Stab., 4, 1 (1982)

63. I.T.Brownlie, and K.U.Ingold, Can. J. Chem, 45, 2427 (1967)

64. B.Felder, R.Schumacher, and K.Sitek, Org. Coat. Plast. Chem., 42, 561 (1980)

65. X.Hu, L.Gu, J.Qi, D.Wang, and M.Cui, Gaofenzi Tongzun, 384 (1982) [CA98:127054z]

66. J.P.T.Jensen, D.J.Carlsson, and D.M.Wiles, Polym. Bull., 9, 321 (1983)

67. D.Bellus, H.Lind, and J.F.Wyatt, J. Chem . Soc. Chem. Comm., 1199 (1972)

68. A.R.Watkins, Chem. Phys. Lett., 29, 526 (1974)

69. J.C.Scaiano, Chem. Phys. Lett., 79, 441 (1981)

70. J.S.Hargreaves, and D.Phillips, Eur. Polym. J., 15, 119 (1979)

71. K.H.Chan, D.J.Carlsson, and D.M.Wiles, J. Polym. Sci. Polym. Lett. Ed., 18, 607 (1980)

72. J.Sedlar, J.Petruj, J.Pac, and A.Zhradnikova, Eur. Polym. J., 16, 663 (1980)

73. J.J.Usilton, and A.R.Patel, Polym. Prepr., 18, 393 (1977)

74. D.W.Grattan, D.J.Carlsson, and D.M.Wiles, Polym. Deg. Stab., 1, 69 (1979)

75. D.J.Carlsson, K.H.Chan, J.Durmis, and D.M.Wiles, J. Polym. Sci. Polym. Chem. Ed., 20, 575 (1982)

76. L.Dulog, and R.Bleher, Makromol. Chem. Rapid Comm.,3, 153 (1982)

77. J.Sedlar, J.Petruj, J.Pac, and A.Zhradnikova, Eur. Polym. J., 16, 659 (1980)

78. O.Cicchetti, and F.Gratini, Eur. Polym. J., 8, 561 (1972)

79. J.C.W.Chien, E.J.Vandenburg, and H.Jabloner, J. Polym. Sci. A1, 6, 381 (1968)

80. N.S.Allen, and J.F.McKellar, Chem. Ind. 537 (1977)

81. Ref.1, p.49

82. N.S.Allen, and J.F.McKellar, J. Appl. Polym. Sci., 22, 3277 (1978)

83. N.S.Allen, J.F.McKellar, and D.Wilson, Polym. Deg. Stab., 1, 205 (1979)

84. E.T.Denisov, In "Developments in Polymer Stabilisation " Vol.3, Ed. G.Scott, Applied Science, London, (1980) p.1

85. K.Murayama, S.Morimura, and T.Yoshioka, Bull. Chem. Soc. Japan, 42, 1640 (1969)

86. D.F.Bowman, T.Gillan, and K.U.Ingold, J. Am. Chem. Soc., 93, 6555 (1971)

87. D.J.Carlsson, K.H.Chan, A.Garton, and D.M.Wiles, Pure Appl. Chem., 52, 389 (1980)

88. J.Durmis, D.J.Carlsson, K.H.Chan, and D.M.Wiles, J. Polym. Sci. Polym. Lett. Ed., 19, 549 (1981)

89. M.V.Sudnik, M.F.Rozantsev, A.B.Shapiro, and E.L.Rozantsev, Bull. Acad. Sci. USSR, 2706 (1976)

90. N.S.Allen, Polym. Deg. Stab., 2, 179 (1980)

91. L.R.Mahoney, G.D.Mindenhall, and K.U.Ingold, J. Am. Chem. Soc., 95, 8610 (1973)

92. D.M.Wiles, and D.J.Carlsson, Polym. Deg. Stab., 3, 61 (1980-81)

93. T. Kurosaki, K.W.Lee, and M.Okawara, J. Polym. Sci. Polym. Chem. Ed., 10, 3295 (1972)

94. G.Chapelet-Letourneax, H.Lemaire, and A.Rassat, Bull. Chim. Soc. Fr., 3283 (1965)

95. J.F.W.Keana, S.B.Keana, and D.Beetham, J. Am. Chem. Soc., 89, 3055 (1967)

96. T.Toda, E.Mori, and K.Murayama, Bull. Chem. Soc. Japan, 45, 1904 (1972)

97. E.J.Rauckman, G.M.Rosen, and M.B.Abou-Donia, Synth. Comm., 5, 409 (1975)

98. J.C.Craig, and K.K.Purushothman, J. Org. Chem., 35, 1721 (1970)

99. I.Gillet, Compt. Rend., 228, 1812 (1949)

100. J.Rigaudy, Pure Appl. Chem., 16, 169 (1968)

101. G.W.Cowell, and J.N.Pitts, J. Am. Chem. Soc., 90, 1106 (1968)

102. J.B.Birks, J.H.Appleyard, and R.Pope, Photochem. Photobiol., 2, 493 (1963)

103. I.B.Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules.", Academic Press, New York, (1965), Graph 69

104. D.Rehm, and A.Weller, Ber. Bunsen. Phys. Chem., 73, 834 (1969)

105. A.Zwieg, and J.B.Gallivan, Mol. Photochem., 6, 397 (1974)

106. S.P.Van, and G.Hammond, J. Am. Chem. Soc., 100, 3895 (1978)

107. A.R.Watkins, Aust. J. Chem., 33, 177 (1980)

108. Ref.1, p.24

109. H.Yoda, J.Tanaka, and S.Nagakura, Bull. Chem. Soc. Japan, 33 1660 (1960)

110. J.B.Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience New York (1971) p.36

111. K.T.Moran, Ph.D. Thesis, St.Andrews, (1982)

112. S.F.Dyke, A.J.Floyd, M.Sainsbury, and R.S.Theobald, "Organic Spectroscopy - An Introduction." 2nd Ed., Longman, London (1978) p.111

113. D.Swern, A.H.Clements, and T.M.Luong, Anal. Chem., 41, 412 (1969)

114. D.J.Carlsson, A.Garton, and D.M.Wiles, Macromol., 9, 695 (1976)

115. R.Hiatt, In "Organic Peroxides" Vol.2, Ed. D.Swern, Wiley -Interscience, london, (1971) p.102

116. F.A.Cotton, and G.Wilkinson, "Advanced Inorganic Chemistry" 3rd Ed., Wiley-Interscience, London, (1972) p.637

117. R.Hiatt, K.C.Irwin, and C.W.Gould, J. Org. Chem., 33, 1430 (1968)

118. E.G.Rosantsev, and V.D.Scholle, Russ. Chem. Rev., 40, 233 (1971)

119. W.P.Griffith, "The Chemistry of the Rarer Platinum Metals", Interscience, London, (1967) p.205

120. O.Cicchetti, M.Dubini, P.Perrini, G.P.Vicario, and E.Bua, Eur. Polym. J., 4, 419 (1968)

121. S.Aiba, M.Ohashi, and S.Y.Huang, Ind. Eng. Chem., 7, 497 (1968)

122. D.J.Carlsson, and D.M.Wiles, J. Macromol. Sci. Rev. Macromol. Chem., C14, 155 (1976)

123. S.Tocker, Makromol. Chem., 101, 23 (1967)

124. K.Matsui, and Y.Ogiwara, J. Macromol. Sci. Chem., A1, 581 (1967)

125. Y.Misutani, and K.Kusumoto, J. Appl. Polym. Sci., 19, 713 (1975)

126. R.J.Roe, H.E.Bair, and C.Gieniewski, J. Appl. Polym. Sci., 18, 834 (1974)

127. H.E.Bair, Polym. Eng. Sci., 13, 435 (1973) [CA80:84022w]

128. A.Tozzi, G.Cantatore, and F.Masima, Text. Res. J., 48 433 (1978)

129. J.E.Wilson, J.Chem. Phys., 22, 334 (1954)

130. C.R.Boss, and J.C.W.Chien, J. Polym. Sci. Polym. Chem. Ed., 4, 1543 (1966)

131. H.H.G.Jellinek, and S.N.Lipovac, Macromol., 3, 237 (1970)

132. N.C.Billingham, and T.J.Walker, J. Polym. Sci. Polym. Chem. Ed., 13, 1209 (1975)

133. J.Crank, "Mathematics of Diffusion." Clarendon Press, (1975)

134. P.Meares, "Polymers : Structure and Bulk Properties.", Van Nostrand, (1965)

135. J.Kresta, J.Majer, and K.Vesely, J. Polym. Sci. C, 22, 329 (1968)

136. A.Tkac, L.Omelka, and J.Holcik, J. Polym. Sci. C, 40, 105 (1973)

137. N.S.Allen, K.O.Fatinikun, and T.J.Henman, Eur. Polym. J., 551 (1983)

138. D.T.Clark, and J.Peeling, Polym. Deg. Stab., 3, 177 (1981)

139. W.H.Richardson, J. Am. Chem. Soc., 87, 247 (1965)

140. R.W.Alder, and R.B.Sessions, In "The Chemistry of Functional Groups Supplement F - The Chemistry of Amino, Nitroso, and Nitro Compounds and Their Derivitives", Ed. S.Patai, Interscience,

New York, (1982) p.793.

141. G.C.Furneaux, K.J.Ledbury, and A.Davis, Polym. Deg. Stab., 3, 431 (1981).

142. W.H.Gibb, and J.R.MacCallum, Eur. Polym. J., 7, 1231 (1971).